Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Metal-free photocleavage of C(non-acyl)-S bond of thioesters for regioselective pyridylthioesterification of styrenes

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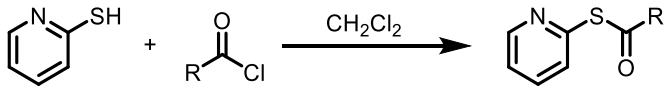
Table of Contents

General Information

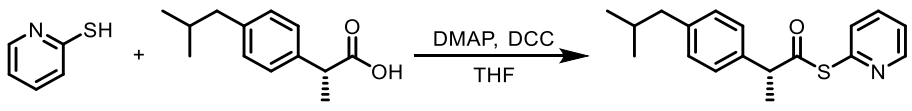
Thiopyridyl esters were synthesized by adapting the reported procedures.[S1,S2] All reagents were used as purchased without further purification. All solvents were obtained from commercial sources and were purified according to standard procedures. Column chromatography was performed on silica gel. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded at ambient temperature on a Varian UNITY plus-400 spectrometer. UV-vis absorption spectra were obtained on a Shimadzu UV-2600 Spectrophotometer. Photoluminescence spectra were measured on a Hitachi F2500 apparatus. High-performance liquid chromatography (HPLC) was conducted on a LC-20AT with MeOH and H_2O as the mobile phase. High resolution mass spectra (HRMS) were obtained with a MICRO TOF-Q III. Infrared (IR) spectra were recorded on a Varian 1000 spectrometer using KBr disks (4000-400 cm^{-1}).

Synthesis of *S*-2-Pyridyl Thioesters 1a-1r, 1t[S1-S7]



To a solution of pyridine-2-thiol (0.333 g, 3.0 mmol, 1.0 equiv) in CH_2Cl_2 (5 mL) was added acyl chloride (3.6 mmol, 1.2 equiv). After the reaction mixture was stirred at room temperature for 1 h, saturated aqueous $NaHCO_3$ (10 mL) was added. The mixture was extracted with CH_2Cl_2 (10 mL × 3). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure to afford a yellow oil. The oil was dissolved in a minimum volume of ethyl acetate and precipitated with petroleum ether. The product was collected by filtration. Compounds **1a-1c**,[S3] **1d**,[S4] **1f**,[S2] **1g-1h**,[S3] **1i**,[S5] **1l-1n**,[S5] **1o**[S6] and **1p**[S7] were characterized by comparing their ^{1}H NMR spectral data with those reported in the literature. New compounds **1e**, **1j**, **1k**, **1q**, **1r**, **1t** were characterized by NMR, IR, MS.

Synthesis of *S*-2-Pyridyl Thioester 1s[S2]



To a solution of 2-thiopyridine (0.66 g, 6.0 mmol, 1.5 equiv) and (*R*)-2-(4-isobutylphenyl)propanoic acid (0.82g, 4.0 mmol, 1.0 equiv) in THF (20 mL) was added 4-dimethylaminopyridine (DMAP, 25 mg, 0.2 mmol, 0.05 equiv.) and dicyclohexylcarbodiimide

(DCC, 1.24 g, 6.0 mmol, 1.5 equiv.) under argon atmosphere. After stirring for 10 h at room temperature, the insoluble dicyclohexylurea was filtered off. The filtrate was concentrated in vacuo. A crude product was purified by column chromatography. Compound **1s** was characterized by comparing its ^{1}H NMR spectral data with the reported in the literature.[S2]

Synthesis of 2s-2v[S8]

To a DMF (5 mL) solution of carboxylic acid (1 mmol, 1.0 equiv) was added K_2CO_3 (0.207 g, 1.5 mmol, 1.5 equiv), KI (0.249 g, 1.5 mmol, 1.5 equiv), and 4-vinylbenzyl chloride (0.168 g, 1.1 mmol, 1.1 equiv). The reaction mixture was stirred for 12 h at room temperature. The mixture was partitioned between water and ethyl acetate. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate. The organic layer was collected, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel using petroleum ether (PE) and ethyl acetate (EA) as eluent. Compound **2s**, **2t** was characterized by comparing its ^{1}H NMR spectral data with the reported in the literature.[S8] New compounds **2u**, **2v** were characterized by NMR, IR, MS.

Gram Scale Reaction

S-(pyridin-2-yl) benzothioate (1.08 g, 5 mmol, 1.0 equiv), styrene (1.56 g, 15 mmol, 3.0 equiv), and $HNEt_2$ (0.366 g, 5 mmol, 1.0 equiv) were weighed into a dried 100 mL flask and degassed, anhydrous DMSO (50 mL) was added. The reaction was stirred under a nitrogen atmosphere and irradiated by 20 W blue LEDs for 24 h through cooling with a fan. Next, 100 mL of water was added, and the mixture was extracted three times with ethyl acetate (3 × 40 mL). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The pure product was obtained by flash column chromatography on silica gel using petroleum ether and ethyl acetate as the eluent: 0.91 g, 57%.

X-Ray Data Collection and Structure Determination

The crystal data of **3aa** and **3ac** were collected on a Rigaku Mercury CCD X-ray diffractometer (3 kV, sealed tube) by using graphite monochromated Mo-Kα (λ = 0.71073 Å), Agilent Xcalibur diffractometer (for **3aa**) or Bruker APEX-II CCD (for **3ac**) using an X-ray source Mo Kα (λ = 0.71073 Å). Single crystals of **3aa** (CCDC 2133458) and **3ac** (CCDC 2133459) were mounted on glass fibers with grease at room temperature (**3ac**) or cooled in a liquid nitrogen stream at 213 K

(**3aa**). The collected data were reduced by using the program CrystalClear (Rigaku and MSC, Ver. 1.3, 2001), Bruker APEX2 or CrysAlisPro, Agilent Technologies (CrysAlis171 .NET, Version 1.171.36.28) and an absorption correction (multi-scan) was applied. The reflection data were also corrected for Lorentz and polarization effects. The crystal structures of **3aa** and **3ac** were solved by direct methods and refined on F2 by full-matrix least-squares methods with the SHELXTL-2014/7 program.[S9] All non-H atoms were refined anisotropically. Pertinent crystal data and collection and refinement parameters for **3aa** and **3ac** are summarized in Table S1.

Table S1. Crystal Data and Structure Refinement for 3aa and 3ac

Empirical formula	$C_{20}H_{17}NOS$	$C_{48}H_{50}N_2O_2S_2$
Formula weight	319.4	751.02
Temperature/K	213	293
Crystal system	monoclinic	monoclinic
Space group (number)	$P2_1/c$	$P2_1/n$
a/Å	9.9510(10)	10.4692(9)
b/Å	17.6043(12)	20.4742(17)
c/Å	10.2940(9)	19.5881(18)
α/ º	90	
β/ º	111.625(11)	97.740(3)
γ/ º	90	
V/Å^3	1676.4(3)	4160.4(6)
Z	4	4
ρ_{calc}/g cm^{-3}	1.266	1.199
μ/mm^{-1}	1.731	0.168
F(000)	672	1600
R_1[a]	0.0760	0.0954
wR_2[b]	0.2123	0.2671
GOF[c]	1.108	1.125

[a]$R = \Sigma F_o|-|F_c||/\Sigma|F_o|$ [b]$R_w = \{w\Sigma(|F_o|-|F_c|)^2/\Sigma w|F_o|^2\}\}^{1/2}$ [c]GOF $= \{\Sigma w(|F_o|-|F_c|)^2/(M-N)\}^{1/2}$, where M is the number of reflections and N is the number of parameters.

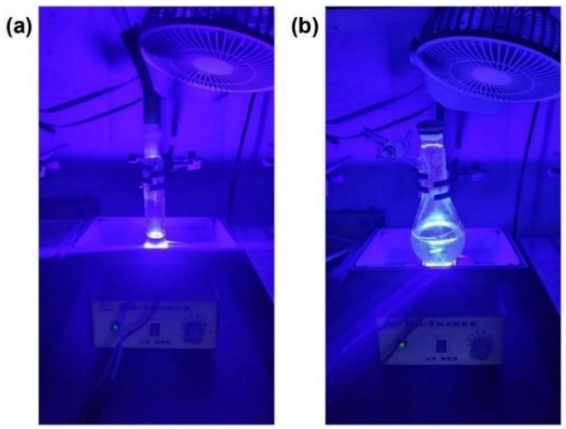
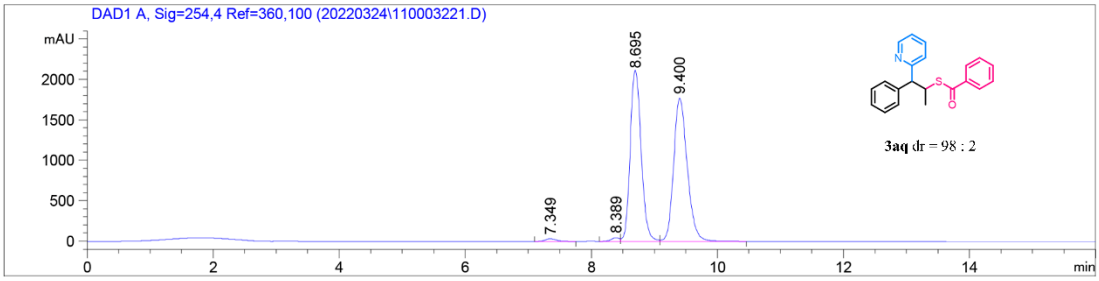
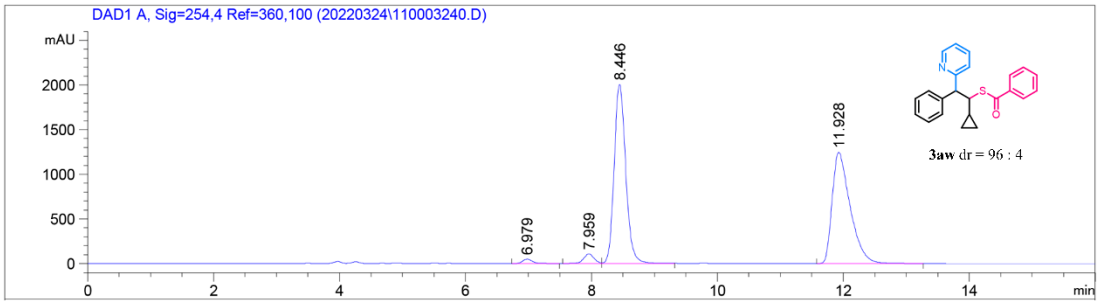


Fig. S1. (a) The reaction set-up with 20 W blue LEDs. (b) The gram scale reaction set-up with 20 W blue LEDs.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.349	BB	0.1971	439.40186	33.48230	0.8272
2	8.389	VV	0.1396	436.92654	47.37429	0.8226
3	8.695	VV	0.1868	2.55730e4	2119.59009	48.1445
4	9.400	VB	0.2316	2.66679e4	1772.15308	50.2057



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.979	VB	0.1824	611.43585	50.81773	1.1642
2	7.959	BV	0.1838	1320.22656	108.64185	2.5138
3	8.446	VB	0.1997	2.57580e4	2006.79175	49.0448
4	11.928	BB	0.3005	2.48297e4	1245.80920	47.2772

Fig. S2. The diastereomeric ratio of **3aq** and **3aw**.

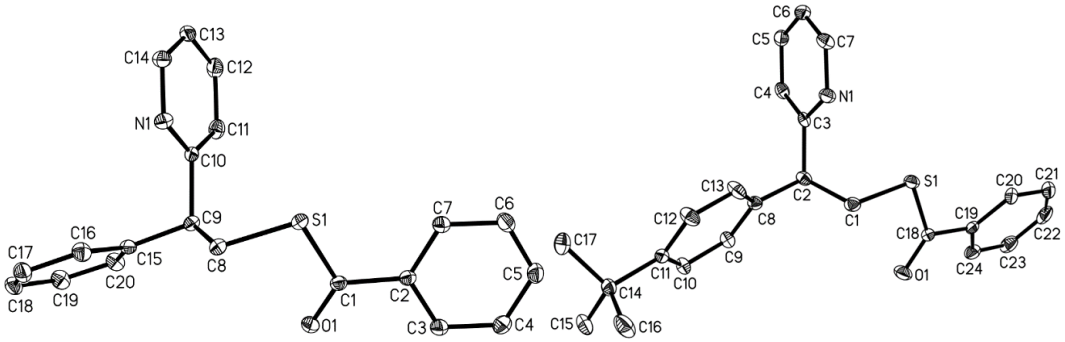


Fig. S3. Molecular structures of **3aa** and **3ac** with 30% thermal probability ellipsoids. All H atoms are omitted for clarity.

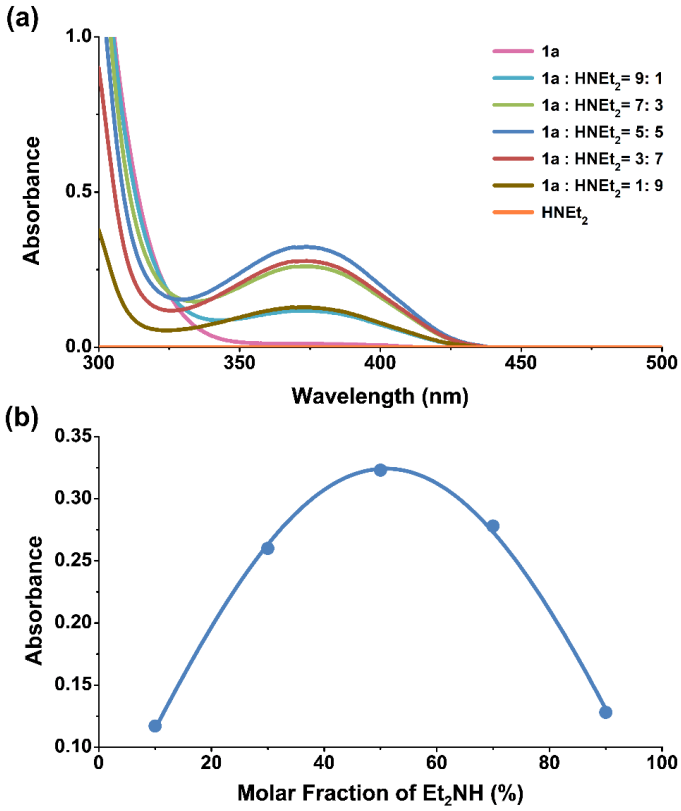


Fig. S4. (a) UV-vis absorption spectra of each mixture for **1a** and $HNEt_2$ (**1a** + $HNEt_2$ = 4×10^{-4} mol L^{-1}) in DMSO. (b) Job's plots of the EDA complex in DMSO.

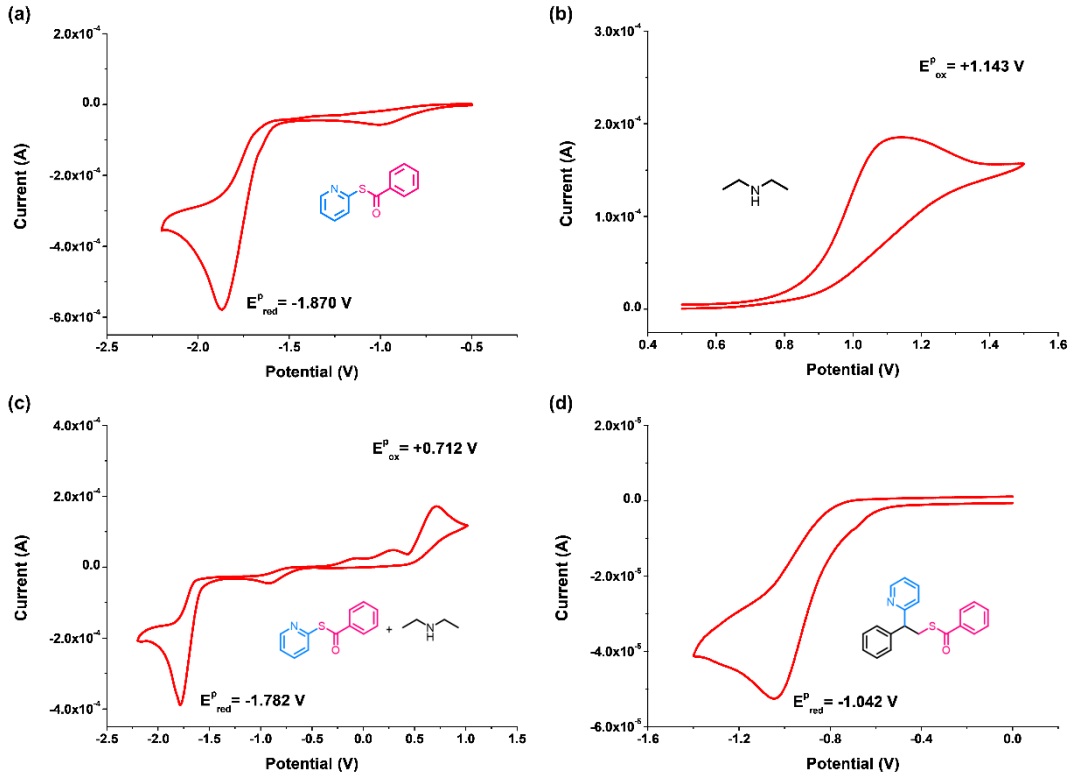


Fig. S5. Cyclic voltammograms of **1a** (a), $HNEt_2$ (b), the mixture of **1a** with $HNEt_2$ (c) and **3aa** (d) using $(n\text{-Bu})_4NPF_6$ as the electrolyte (0.05 M) in DMF at 100 mV/s scan rate. Working electrode: glassy carbon electrode tip (3 mm diameter); Counter electrode: platinum wire; Reference electrode: Saturated Calomel Electrode (SCE).

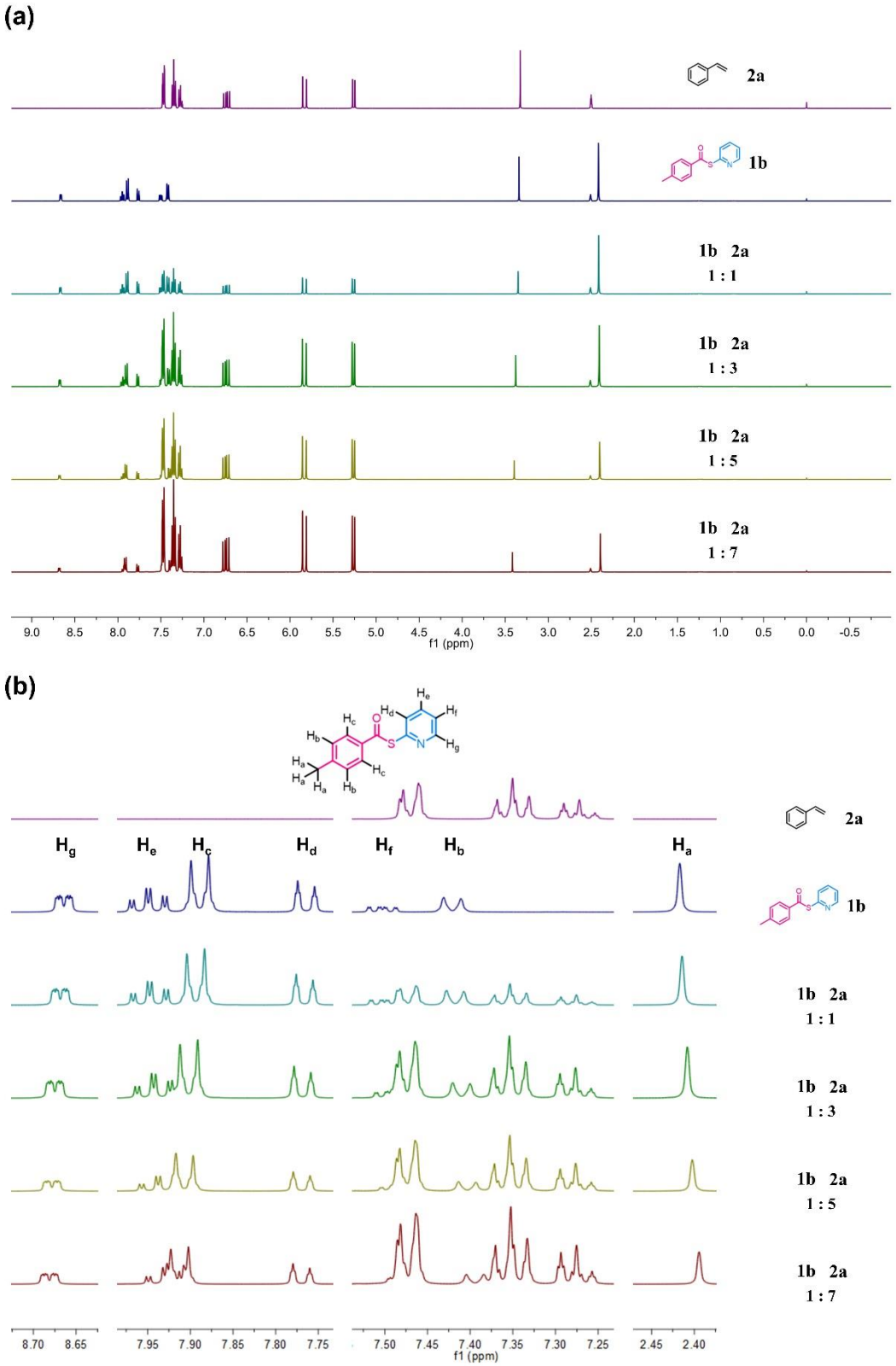


Fig. S6. ^{1}H NMR spectra showing different ratios of **1b** (0.08 mmol) : **2a** in DMSO-d_6. (a) Full ^{1}H NMR spectra. (b) Selected region of the ^{1}H NMR spectral window showing diagnostic signals for **1b**.

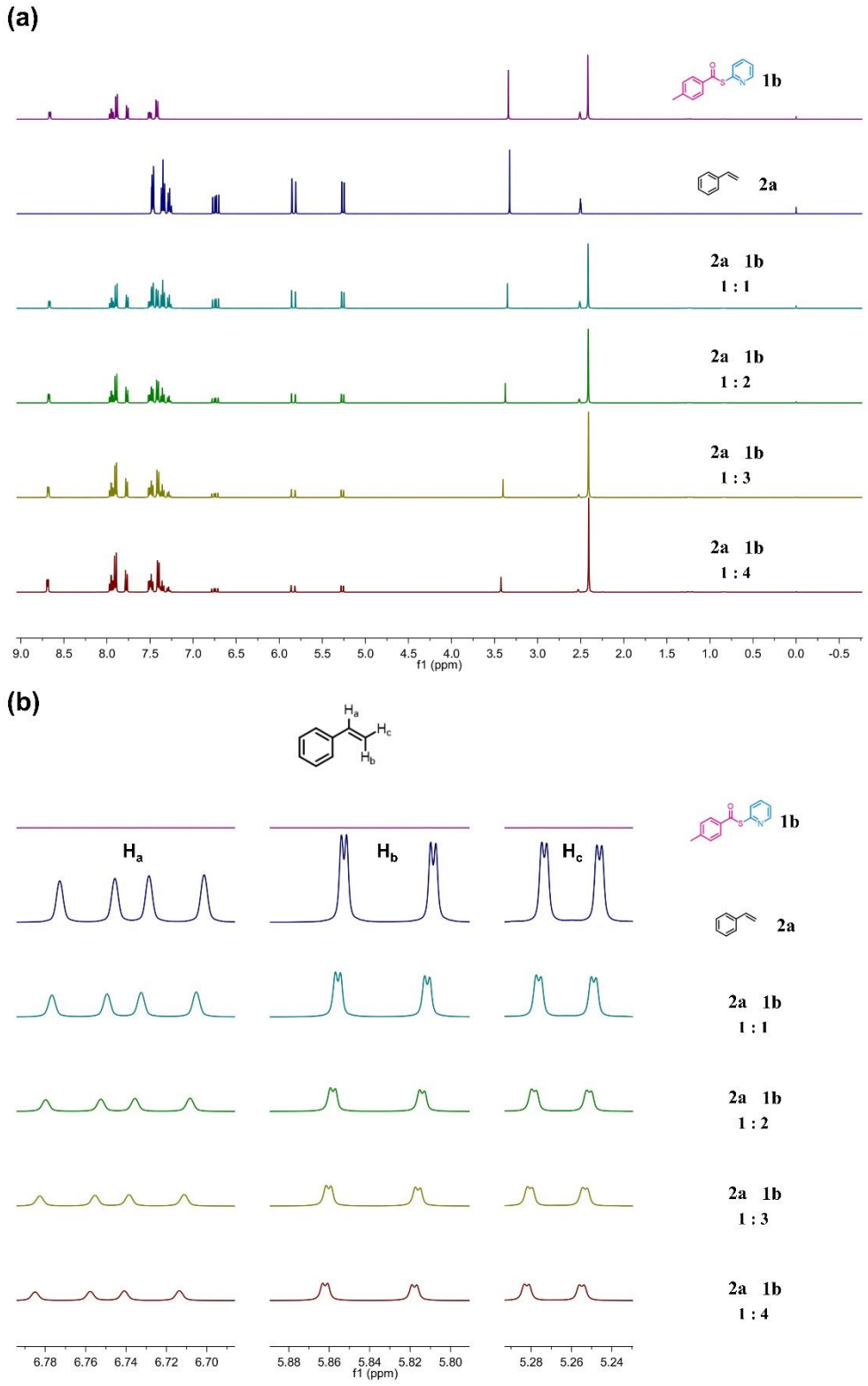


Fig. S7. ^{1}H NMR spectra showing different ratios of **2a** (0.08 mmol) : **1b** in DMSO-d_6. (a) Full ^{1}H NMR spectra. (b) Selected region of the ^{1}H NMR spectral window showing diagnostic signals for **2a**.

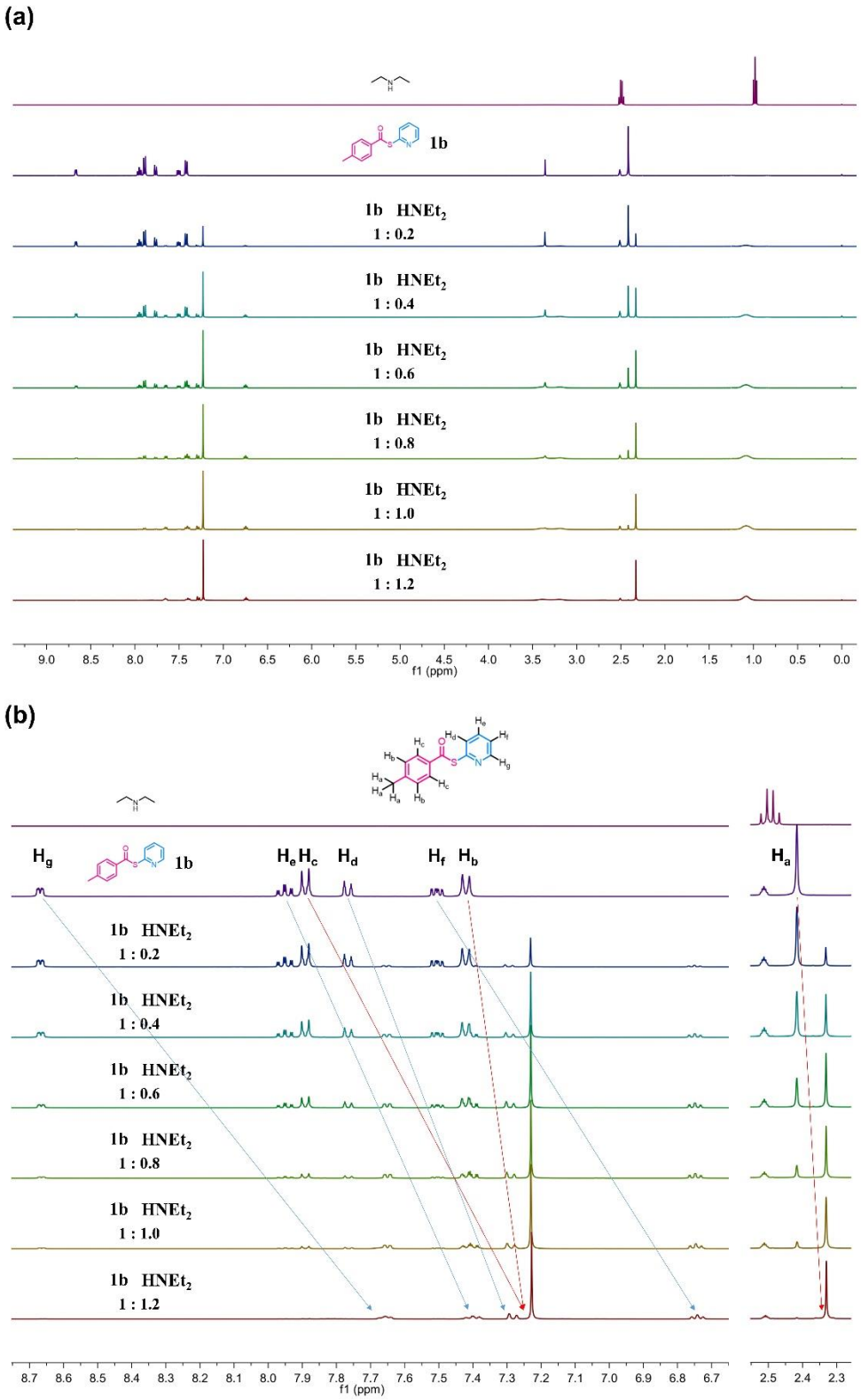


Fig. S8. ^{1}H NMR spectra showing different ratios of **1b** (0.10 mmol) : $HNEt_2$ in DMSO-d_6. (a) Full ^{1}H NMR spectra. (b) Selected region of the ^{1}H NMR spectral window showing diagnostic signals for **1b**.

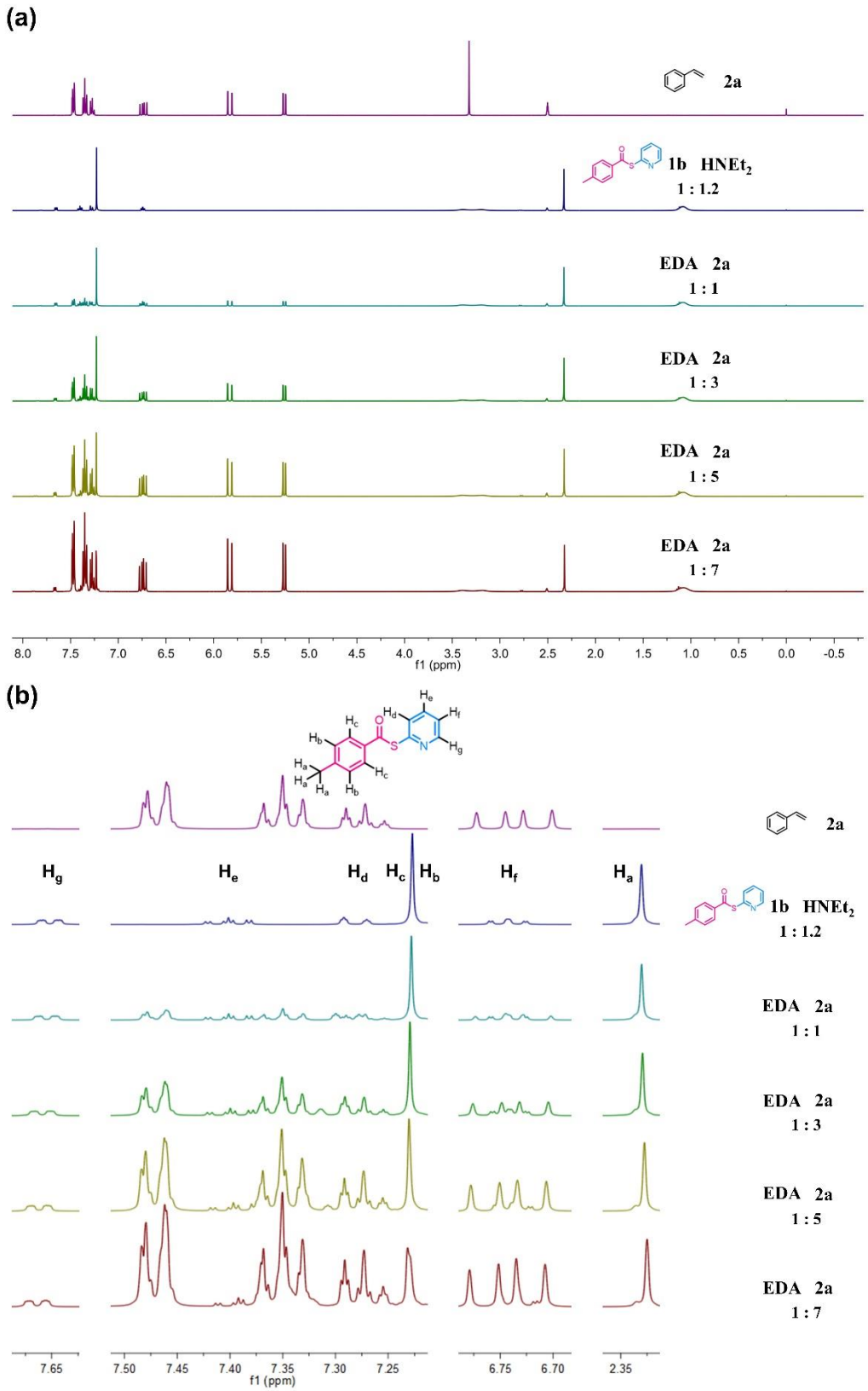


Fig. S9. ^{1}H NMR spectra showing different ratios of EDA (0.10 mmol **1b**, 0.12 mmol $HNEt_2$) : **2a** in DMSO-d_6. (a) Full ^{1}H NMR spectra. (b) Selected region of the ^{1}H NMR spectral window showing diagnostic signals for EDA.

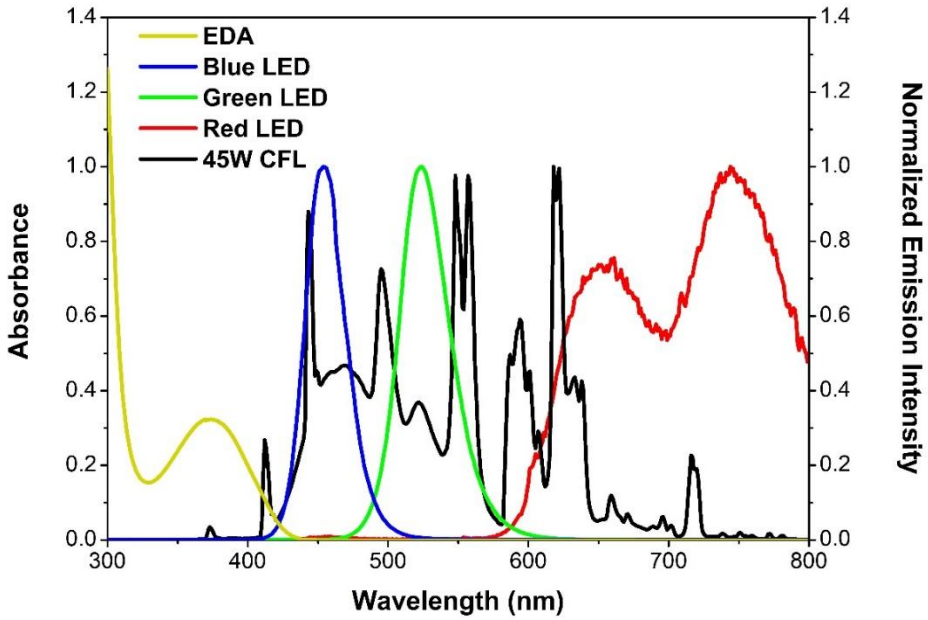


Fig. S10. The absorption spectrum of EDA (**1a** + $HNEt_2$) and the emission spectra of different lights.

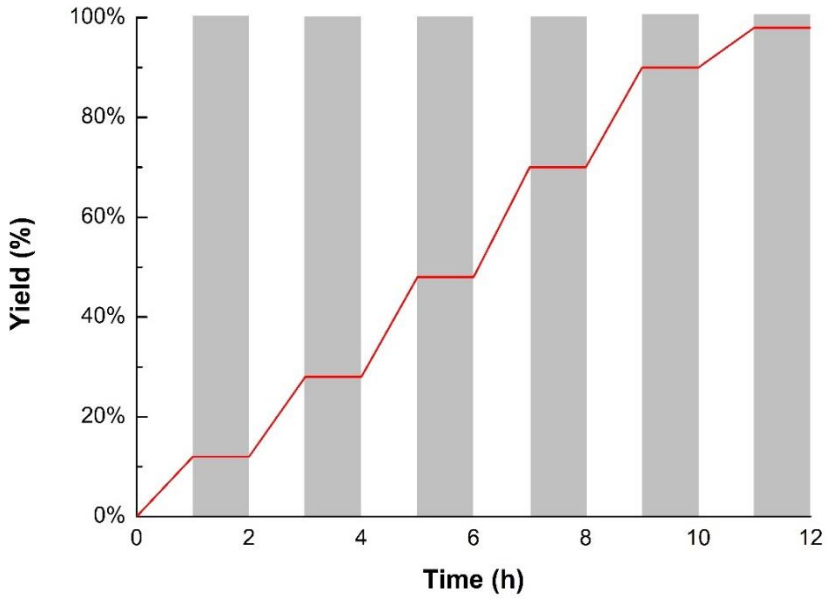
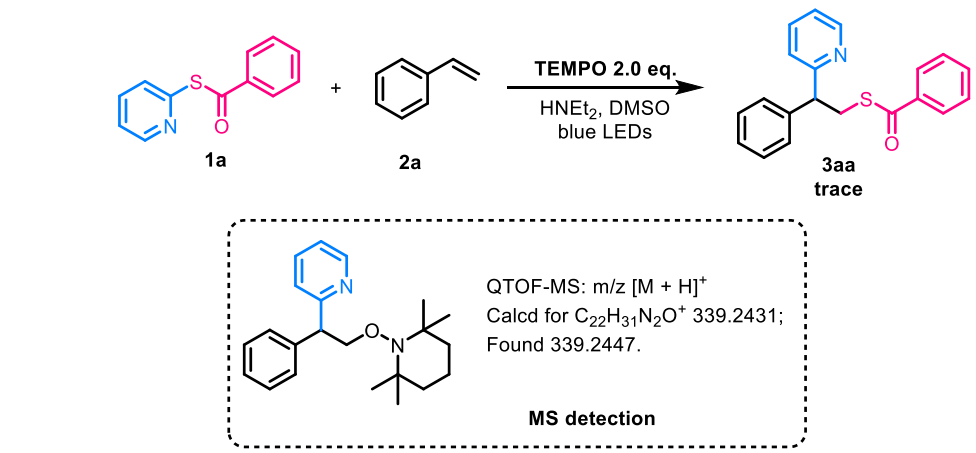


Fig. S11. Profile of the reaction with the light off/on over time.

Mechanistic Studies



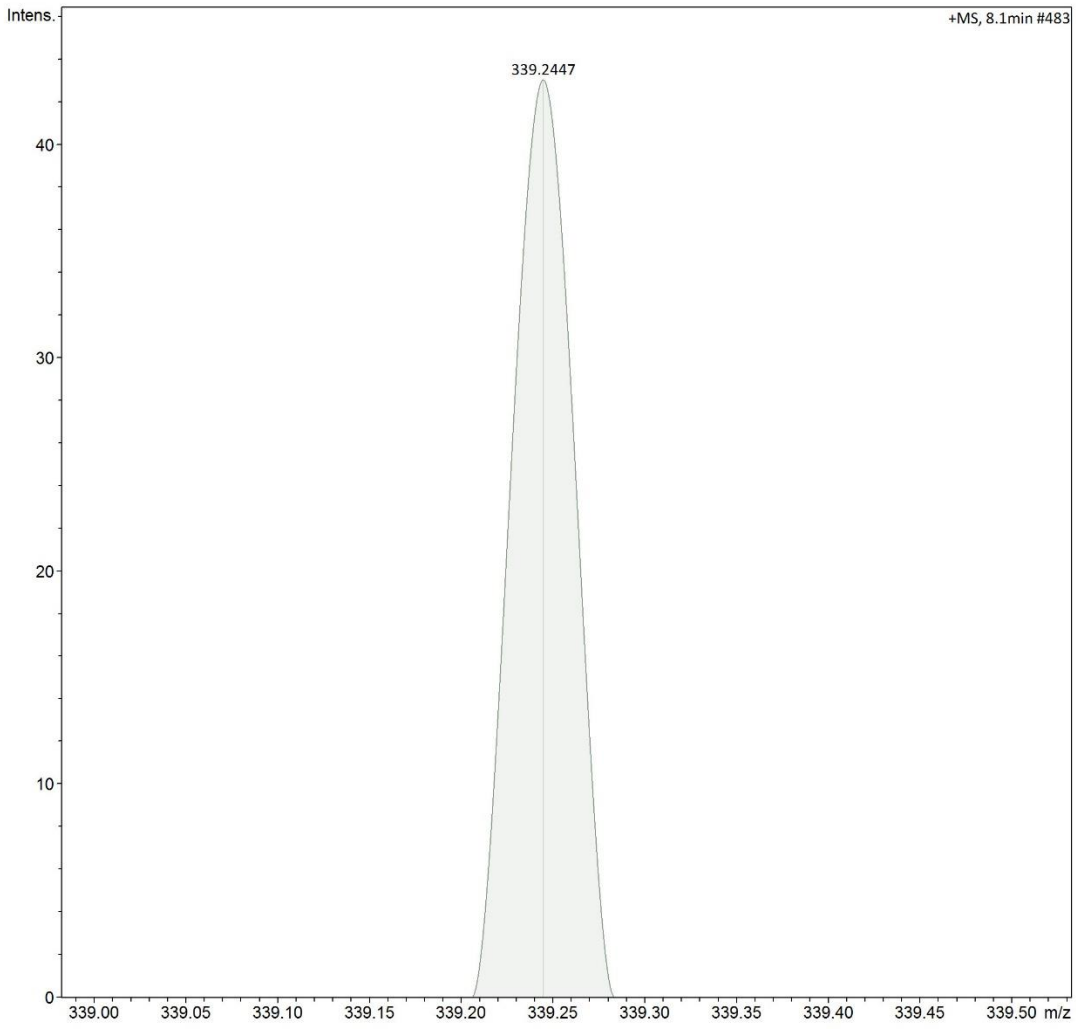
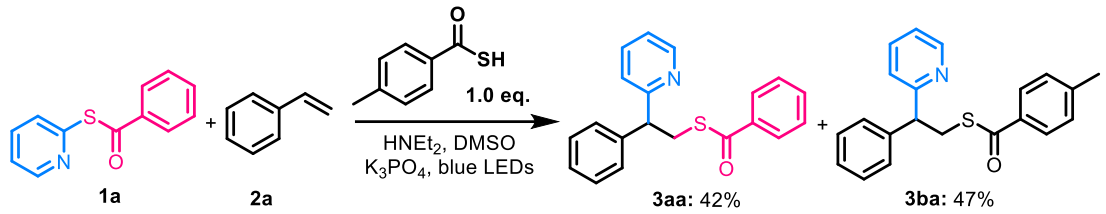


Fig. S12. Mass spectroscopy (MS) of [2-(1-phenyl-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethyl)pyridine



A 10 mL test tube was charged with styrene (0.6 mmol, 3.0 equiv), *S*-(pyridin-2-yl) benzothioate (0.2 mmol, 1.0 equiv), 4-methylbenzothioic *S*-acid (0.2 mmol, 1.0 equiv), K_3PO_4 (0.04 mmol, 0.2 equiv), $HNEt_2$ (0.2 mmol, 1.0 equiv) and dried DMSO (2 mL) under a nitrogen atmosphere. The reaction mixture was stirred and irradiated with 20 W blue LEDs for 6 h through cooling with a fan. Next, 3 mL of water was added, and the mixture was extracted three times with EA (3 × 3 mL). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The pure product was obtained by flash column chromatography on silica gel using PE and EA as an eluent. The product was a mixture of **3aa** and **3ba** found by ^{1}H NMR (Figure S12).

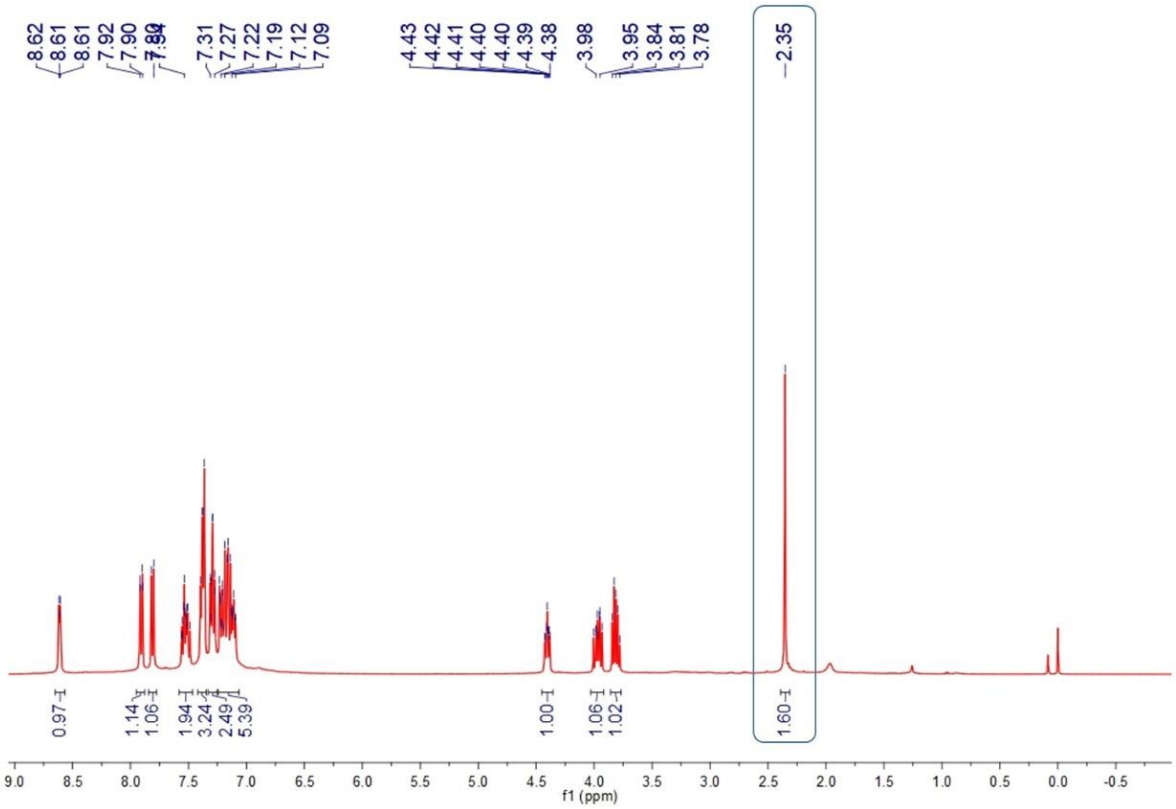
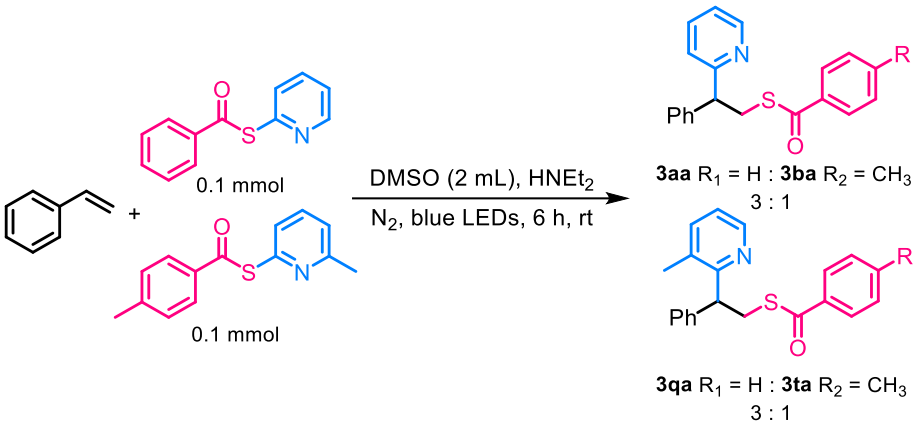


Fig. S13. ^{1}H NMR spectrum of the mixture of **3aa** and **3ba**.



A 10 mL test tube was charged with styrene (0.6 mmol, 3.0 equiv), *S*-(pyridin-2-yl) benzothioate (0.1 mmol, 0.5 equiv), *S*-(6-methylpyridin-2-yl) 4-methylbenzothioate (0.1 mmol, 0.5 equiv), $HNEt_2$ (0.2 mmol, 1.0 equiv) and dried DMSO (2 mL) under a nitrogen atmosphere. The reaction mixture was stirred and irradiated with 20 W blue LEDs for 6 h through cooling with a fan. Next, 3 mL of water was added, and the mixture was extracted three times with EA (3 × 3 mL). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The pure product was obtained by flash column chromatography on silica gel using PE and EA as an eluent. The product was a mixture of **3aa, 3ba, 3qa** and **3ta** found by ^1H NMR (Figure S13 and Figure S14).

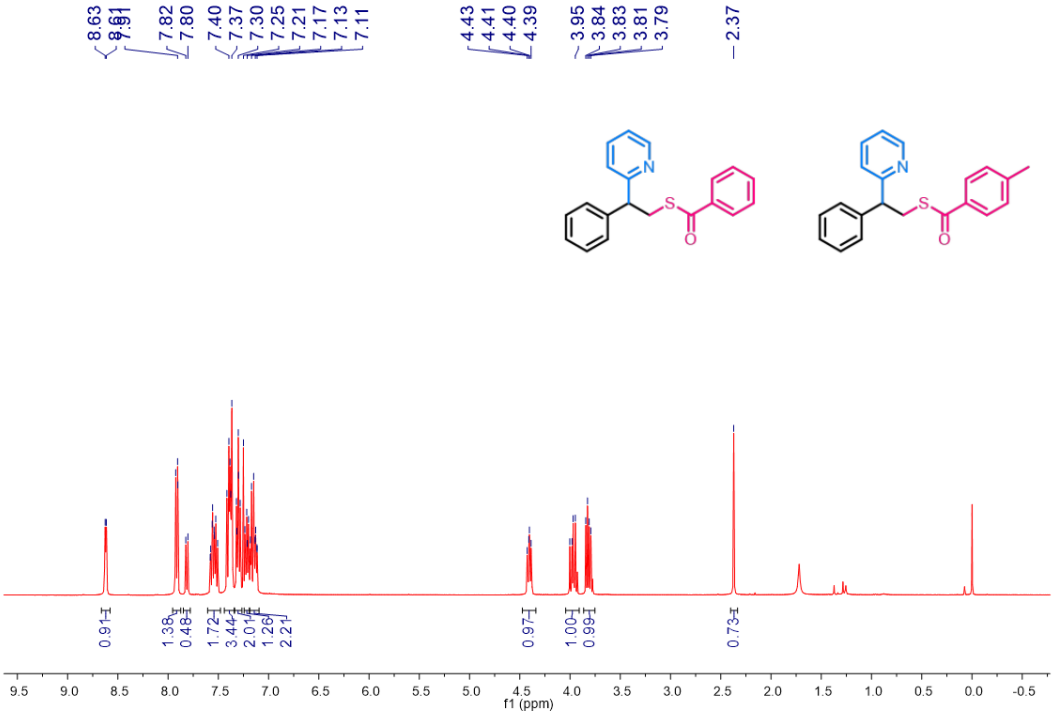


Fig. S14. ^1H NMR spectrum of the mixture of **3aa** and **3ba**.

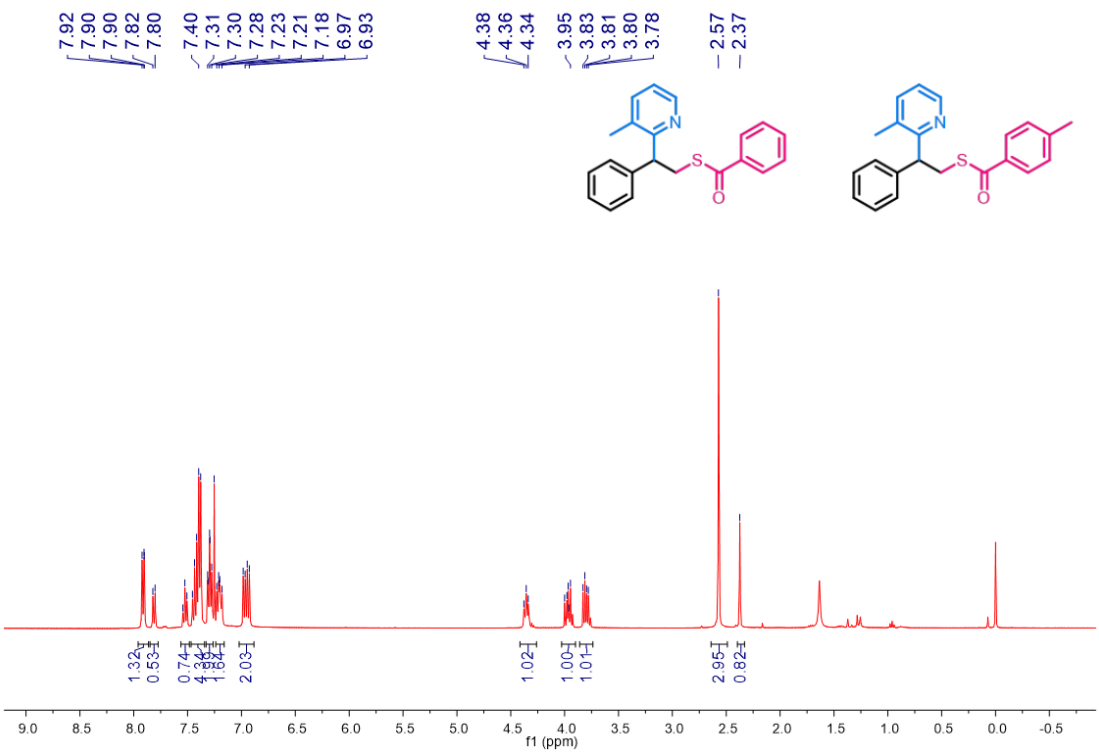
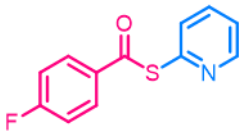


Fig. S15. ^{1}H NMR spectrum of the mixture of **3qa** and **3ta**.

NMR Data of Unknown Substrates and Products

***S*-(pyridin-2-yl) 4-fluorobenzothioate (1e)**



Following the General Procedure A with the corresponding 4-fluorobenzoyl chloride (3.6 mmol) and pyridine-2-thiol (3.0 mmol). The crude product was recrystallized by PE, to yield the white solid **1e** (559 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 4.5 Hz, 1H), 8.11–7.99 (m, 2H), 7.79 (td, *J* = 7.7, 1.7 Hz, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.37–7.31 (m, 1H), 7.17 (t, *J* = 8.6 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 187.9, 166.2 (d, $^{1}J_{C\text{-}F}$ = 256.1 Hz), 151.0, 150.6, 137.3, 132.9 (d, $^{4}J_{C\text{-}F}$ = 3.0 Hz), 130.9, 130.2 (d, $^{3}J_{C\text{-}F}$ = 9.5 Hz), 123.8, 116.1 (d, $^{2}J_{C\text{-}F}$ = 22.1 Hz).

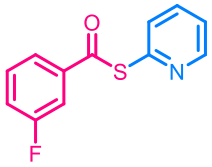
^{19}F NMR (377 MHz, $CDCl_3$) δ -103.58.

IR (KBr disc, cm^{-1}): 3059, 2350, 1671, 1594, 1572, 1499, 1452, 1420, 1408, 1294, 1200, 1151, 1118, 1097, 1080, 902, 839, 723, 476, 457, 442, 426, 414, 405.

m.p. 71.1-73.8 ℃.

QTOF-MS: *m/z* $[M + H]^+$ Calcd for $C_{12}H_9FNOS^+$ 234.0383; Found 234.0380.

***S*-(pyridin-2-yl) 3-fluorobenzothioate (1j)**



Following the General Procedure A with the corresponding 3-fluorobenzoyl chloride (3.6 mmol) and pyridine-2-thiol (3.0 mmol). The crude product was recrystallized by PE, to yield the white solid **1j** (454 mg, 65%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73–8.64 (m, 1H), 7.86–7.76 (m, 2H), 7.70 (ddd, *J* = 9.1, 6.6, 5.0 Hz, 2H), 7.48 (td, *J* = 8.0, 5.5 Hz, 1H), 7.38–7.28 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 187.2 (d, $^{4}J_{C\text{-}F}$ = 2.7 Hz), 161.7 (d, $^{1}J_{C\text{-}F}$ = 249.0 Hz), 149.8, 149.6, 137.5 (d, $^{3}J_{C\text{-}F}$ = 6.6 Hz), 136.3, 129.5 (d, $^{3}J_{C\text{-}F}$ = 7.9 Hz), 129.5, 122.8, 122.3 (d, $^{4}J_{C\text{-}F}$ = 3.3 Hz), 119.9 (d, $^{2}J_{C\text{-}F}$ = 21.6 Hz), 113.4 (d, $^{2}J_{C\text{-}F}$ = 23.2 Hz).

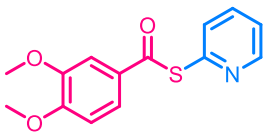
^{19}F NMR (377 MHz, $CDCl_3$) δ -111.08.

IR (KBr disc, cm^{-1}): 3086, 3067, 3044, 2349, 1974, 1789, 1676, 1609, 1561, 1482, 1420, 1284, 1278, 1243, 1170, 1110, 1077, 1044, 984, 897, 795, 777, 742, 724, 693, 617, 573, 432, 413, 404.

m.p.: 39.3-40.1 ℃.

QTOF-MS: *m/z* $[M + H]^+$ Calcd for $C_{12}H_9FNOS^+$ 234.0383; Found 234.0378.

***S*-(pyridin-2-yl) 3,4-dimethoxybenzothioate (1k)**



Following the General Procedure A with the corresponding 3,4-dimethoxybenzoyl chloride (3.6 mmol) and pyridine-2-thiol (3.0 mmol). The crude product was recrystallized by PE, to yield the white solid **1k** (742 mg, 90%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 4.1 Hz, 1H), 7.83–7.70 (m, 3H), 7.50 (d, *J* = 2.0 Hz, 1H), 7.36–7.30 (m, 1H), 6.94 (d, *J* = 8.5 Hz, 1H), 3.97 (s, 3H), 3.94 (s, 3H).

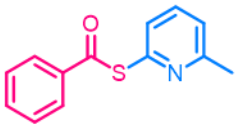
^{13}C NMR (101 MHz, $CDCl_3$) δ 187.9, 153.9, 151.7, 150.5, 149.1, 137.1, 130.9, 129.5, 123.5, 122.3, 110.4, 109.8, 56.2, 56.1.

IR (KBr disc, cm^{-1}): 3012, 2955, 2933, 2381, 2350, 2327, 1668, 1592, 1581, 1564, 1515, 1449, 1421, 1346, 1267, 1243, 1146, 1119, 1012, 987, 969, 863, 803, 761, 737, 723, 675, 618, 596, 455, 433, 420, 403.

m.p.: 89.1-90.2 ℃.

QTOF-MS: *m/z* $[M + H]^+$ Calcd for $C_{14}H_{14}NO_3S^+$ 276.0689; Found 276.0688.

_S_-(6-methylpyridin-2-yl) benzothioate (1q)



Following the General Procedure A with the corresponding benzoyl chloride (0.48 mmol) and 6-methylpyridine-2-thiol (0.4 mmol). The crude product was recrystallized by PE, to yield the white solid **1q** (77.9 mg, 85%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.2 Hz, 2H), 7.67 (t, *J* = 7.7 Hz, 1H), 7.63–7.57 (m, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.19 (d, *J* = 7.6 Hz, 1H), 2.60 (s, 3H).

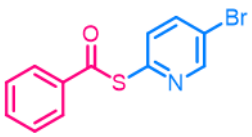
^{13}C NMR (101 MHz, $CDCl_3$) δ 189.6, 159.8, 150.1, 137.4, 136.6, 133.8, 128.8, 128.0, 127.6, 123.4, 24.4.

IR (KBr disc, cm^{-1}): 3060, 1785, 1708, 1676, 1583, 1559, 1443, 1385, 1313, 1206, 1170, 1139, 1039, 992, 894, 863, 776, 707, 683, 645, 616, 547, 482.

m.p.: 87.2-88.4 ℃.

QTOF-MS: *m/z* $[M + H]^+$ Calcd for $C_{13}H_{12}NOS^+$ 230.0634; Found 230.0633.

_S_-(5-bromopyridin-2-yl) benzothioate (1r)



Following the General Procedure A with the corresponding benzoyl chloride (0.48 mmol) and 5-bromopyridine-2-thiol (0.4 mmol). The crude product was recrystallized by PE, to yield the white solid **1r** (94.1 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 2.3 Hz, 1H), 8.05–7.97 (m, 2H), 7.91 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.63 (dd, *J* = 7.9, 4.9 Hz, 2H), 7.50 (t, *J* = 7.8 Hz, 2H).

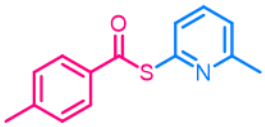
^{13}C NMR (101 MHz, $CDCl_3$) δ 188.7, 151.6, 150.0, 139.8, 136.3, 134.1, 131.7, 128.9, 127.6, 121.3.

IR (KBr disc, cm^{-1}): 3052, 2349, 2330, 2298, 1665, 1593, 1579, 1550, 1439, 1312, 1261, 1231, 1201, 1144, 1130, 1105, 1000, 905, 827, 803, 769, 728, 681, 640, 485, 440, 424.

m.p.: 93.8-95.2 ℃.

QTOF-MS: *m/z* $[M + H]^+$ Calcd for $C_{12}H_9BrNOS^+$ 293.9583; Found 293.9583.

S-(6-methylpyridin-2-yl) 4-methylbenzothioate (1t)



Following the General Procedure A with the corresponding 4-methylbenzoyl chloride (0.48 mmol) and 6-methylpyridine-2-thiol (0.4 mmol). The crude product was recrystallized by PE, to yield the white solid **1t** (77.8 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.0 Hz, 2H), 7.66 (td, *J* = 7.7, 1.3 Hz, 1H), 7.54 (d, *J* = 7.7 Hz, 1H), 7.27 (d, *J* = 8.6 Hz, 2H), 7.18 (d, *J* = 7.7 Hz, 1H), 2.60 (s, 3H), 2.42 (s, 3H).

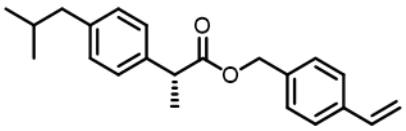
^{13}C NMR (101 MHz, $CDCl_3$) δ 189.1, 159.7, 150.4, 144.8, 137.3, 134.1, 129.5, 128.0, 127.7, 123.3, 24.4, 21.7.

IR (KBr disc, cm^{-1}): 3327, 3118, 3035, 2920, 2857, 2726, 2011, 1783, 1669, 1605, 1573, 1441, 1409, 1307, 1249, 1205, 1167, 1137, 1040, 999, 891, 854, 812, 784, 715, 681, 632.

m.p.: 96.4-98.2 ℃.

QTOF-MS: *m/z* $[M + H]^+$ Calcd for $C_{14}H_{14}NOS^+$ 244.0791; Found 244.0794.

4-vinylbenzyl (*R*)-2-(4-isobutylphenyl)propanoate (2u)



Following the General Procedure C with the corresponding (*R*)-2-(4-isobutylphenyl)propanoic acid (1.0 mmol) and 4-vinylbenzyl chloride (1.1 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 100/1) as an eluent, to yield the transparent oil **2u** (274 mg, 85%).

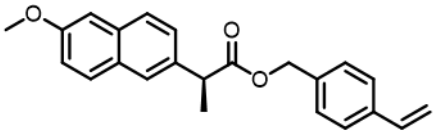
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.29 (m, 2H), 7.18 (dd, *J* = 9.8, 8.2 Hz, 4H), 7.08 (d, *J* = 8.1 Hz, 2H), 6.68 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.72 (dd, *J* = 17.6, 0.7 Hz, 1H), 5.23 (dd, *J* = 10.9, 0.7 Hz, 1H), 5.08 (d, *J* = 1.3 Hz, 2H), 3.74 (q, *J* = 7.2 Hz, 1H), 2.44 (d, *J* = 7.2 Hz, 2H), 1.84 (dp, *J* = 13.6, 6.8 Hz, 1H), 1.50 (d, *J* = 7.2 Hz, 3H), 0.90 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.5, 140.6, 137.6, 137.4, 136.4, 135.7, 129.4, 128.1, 127.3, 126.3, 114.2, 66.1, 45.2, 45.1, 30.2, 22.4, 18.4.

IR (KBr disc, cm^{-1}): 2954, 2868, 2350, 1733, 1630, 1514, 1458, 1421, 1407, 1378, 1319, 1234, 1199, 1156, 1117, 1092, 1073, 1055, 1032, 989, 961, 942, 909, 847, 826, 800, 477, 464, 456, 432, 416.

QTOF-MS: *m/z* $[M + H]^+$ Calcd for $C_{22}H_{27}O_2^+$ 323.2006; Found 323.1998.

4-vinylbenzyl (*S*)-2-(6-methoxynaphthalen-2-yl)propanoate (2v)



Following the General Procedure C with the corresponding (*S*)-2-(6-methoxynaphthalen-2-yl)propanoic acid (1.0 mmol) and 4-vinylbenzyl chloride (1.1 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 100/1) as an eluent, to yield the transparent oil **2v** (242 mg, 70%).

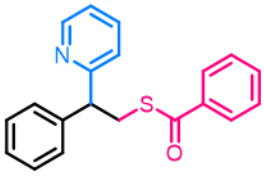
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (t, *J* = 9.2 Hz, 2H), 7.63 (s, 1H), 7.39 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.16–7.08 (m, 2H), 6.68 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.72 (d, *J* = 17.6 Hz, 1H), 5.24 (d, *J* = 10.9 Hz, 1H), 5.09 (q, *J* = 12.5 Hz, 2H), 3.93–3.86 (m, 4H), 1.58 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.5, 157.6, 137.4, 136.4, 135.5, 135.5, 133.7, 129.3, 128.9, 128.3, 127.2, 126.3, 126.0, 119.0, 114.3, 105.6, 66.3, 55.3, 45.5, 18.5.

IR (KBr disc, cm^{-1}): 2991, 2971, 2929, 2853, 2350, 1741, 1629, 1603, 1513, 1376, 1329, 1266, 1177, 1149, 1091, 1078, 1027, 917, 856, 824, 793, 748, 728, 684, 478, 464, 457, 438, 419, 404.

QTOF-MS: *m/z* $[M + H]^+$ Calcd for $C_{23}H_{23}O_3^+$ 347.1642; Found 347.1645.

***S*-(2-phenyl-2-(pyridin-2-yl)ethyl) benzothioate (3aa)**



Following the General Procedure with the corresponding *S*-(pyridin-2-yl) benzothioate (0.2 mmol) and styrene (0.6 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 50/1) as an eluent, to yield the white solid **3aa** (58.7 mg, 92%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (dd, *J* = 4.8, 0.8 Hz, 1H), 7.92 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.60–7.50 (m, 2H), 7.43–7.35 (m, 4H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.25–7.19 (m, 1H), 7.14 (ddd, *J* = 9.2, 5.9, 4.6 Hz, 2H), 4.41 (dd, *J* = 8.8, 6.8 Hz, 1H), 3.98 (dd, *J* = 13.3, 8.9 Hz, 1H), 3.82 (dd, *J* = 13.3, 6.7 Hz, 1H).

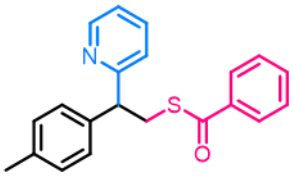
^{13}C NMR (101 MHz, $CDCl_3$) δ 192.1, 161.5, 149.3, 142.5, 137.1, 136.5, 133.3, 128.7, 128.5, 128.1, 127.2, 127.0, 123.8, 121.8, 53.0, 33.7.

IR (KBr disc, cm^{-1}): 2960, 2923, 2360, 1655, 1588, 1571, 1492, 1471, 1432, 1201, 1173, 1159, 1147, 1077, 999, 912, 836, 800, 774, 758, 686, 496, 477, 469, 437, 431, 424, 417, 404.

m.p.: 85.2-86.5 ℃.

QTOF-MS: *m/z* $[M + H]^+$ Calcd for $C_{20}H_{18}NOS^+$ 320.1104; Found 320.1090.

S-(2-(pyridin-2-yl)-2-(*p*-tolyl)ethyl) benzothioate (3ab)



Following the General Procedure with the corresponding *S*-(pyridin-2-yl) benzothioate (0.2 mmol) and 1-methyl-4-vinylbenzene (0.6 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 50/1) as an eluent, to yield the white solid **3ab** (63.3 mg, 95%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (dd, *J* = 4.9, 0.8 Hz, 1H), 7.92 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.55 (td, *J* = 7.7, 1.9 Hz, 1H), 7.52 (ddd, *J* = 7.0, 2.5, 1.3 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 1H), 7.14–7.09 (m, 3H), 4.38 (dd, *J* = 8.7, 7.0 Hz, 1H), 3.96 (dd, *J* = 13.3, 8.8 Hz, 1H), 3.80 (dd, *J* = 13.3, 6.9 Hz, 1H), 2.30 (s, 3H).

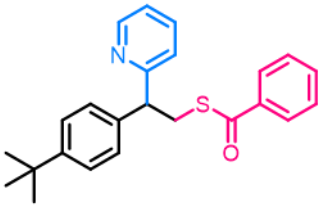
^{13}C NMR (101 MHz, $CDCl_3$) δ 192.1, 161.7, 149.2, 139.5, 137.1, 136.6, 136.5, 133.3, 129.4, 128.5, 128.0, 127.3, 123.7, 121.7, 52.6, 33.8, 21.1.

IR (KBr disc, cm^{-1}): 3361, 2978, 2904, 2360, 2336, 1655, 1589, 1512, 1431, 1399, 1205, 1049, 906, 882, 818, 748, 721, 687, 610, 527, 490, 452, 420.

m.p.: 63.6-64.1 ℃.

QTOF-MS: *m/z* $[M + H]^+$ Calcd for $C_{21}H_{20}NOS^+$ 334.1260; Found 334.1248.

S-(2-(4-(*tert*-butyl)phenyl)-2-(pyridin-2-yl)ethyl) benzothioate (3ac)



Following the General Procedure with the corresponding *S*-(pyridin-2-yl) benzothioate (0.2 mmol) and 1-(*tert*-butyl)-4-vinylbenzene (0.6 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 50/1) as an eluent, to yield the white solid **3ac** (72.0 mg, 96%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (dd, *J* = 4.9, 0.9 Hz, 1H), 7.92 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.56 (td, *J* = 7.7, 1.9 Hz, 1H), 7.53 (t, *J* = 8.0 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.35–7.27 (m, 4H), 7.17 (d, *J* = 7.8 Hz, 1H), 7.13 (ddd, *J* = 7.5, 4.9, 1.0 Hz, 1H), 4.38 (dd, *J* = 9.2, 6.4 Hz, 1H), 3.96 (dd, *J* = 13.3, 9.2 Hz, 1H), 3.81 (dd, *J* = 13.3, 6.4 Hz, 1H), 1.29 (s, 9H).

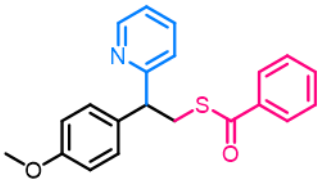
^{13}C NMR (101 MHz, $CDCl_3$) δ 192.1, 161.7, 149.7, 149.2, 139.4, 137.2, 136.5, 133.2, 128.5, 127.6, 127.2, 125.5, 123.8, 121.7, 52.5, 34.4, 33.8, 31.3.

IR (KBr disc, cm^{-1}): 3056, 2961, 2905, 2869, 2361, 1661, 1586, 1511, 1469, 1413, 1364, 1268, 1205, 1175, 1108, 1050, 909, 831, 753, 689, 648, 615, 569, 441, 420.

m.p.: 95.6-96.9 ℃.

QTOF-MS: *m/z* $[M + H]^+$ Calcd for $C_{24}H_{26}NOS^+$ 376.1730; Found 376.1746.

S-(2-(4-methoxyphenyl)-2-(pyridin-2-yl)ethyl) benzothioate (3ad)



Following the General Procedure with the corresponding *S*-(pyridin-2-yl) benzothioate (0.2 mmol) and 1-methoxy-4-vinylbenzene (0.6 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 50/1) as an eluent, to yield the transparent oil **3ad** (67.0 mg, 96%).

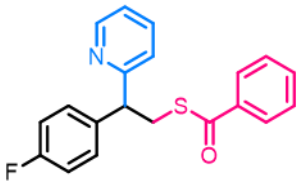
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (ddd, *J* = 4.8, 1.6, 0.7 Hz, 1H), 7.91 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.54 (td, *J* = 7.7, 1.9 Hz, 1H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.32–7.26 (m, 2H), 7.14 (d, *J* = 7.9 Hz, 1H), 7.11 (ddd, *J* = 7.5, 5.0, 1.1 Hz, 1H), 6.87–6.81 (m, 2H), 4.36 (dd, *J* = 8.6, 7.0 Hz, 1H), 3.95 (dd, *J* = 13.3, 8.7 Hz, 1H), 3.78 (dd, *J* = 13.3, 6.9 Hz, 1H), 3.75 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.1, 161.8, 158.6, 149.2, 137.2, 136.5, 134.7, 133.3, 129.1, 128.5, 127.2, 123.6, 121.7, 114.0, 55.2, 52.2, 33.9.

IR (KBr disc, cm^{-1}): 3060, 3005, 2933, 2835, 2350, 1656, 1609, 1588, 1510, 1471, 1448, 1433, 1303, 1247, 1205, 1175, 1035, 995, 908, 830, 796, 773, 748, 688, 648, 614, 568, 537, 464, 457, 432, 413, 403.

QTOF-MS: *m/z* $[M + H]^+$ Calcd for $C_{21}H_{20}NO_2S^+$ 350.1209; Found 350.1182.

S-(2-(4-fluorophenyl)-2-(pyridin-2-yl)ethyl) benzothioate (3ae)



Following the General Procedure with the corresponding *S*-(pyridin-2-yl) benzothioate (0.2 mmol) and 1-fluoro-4-vinylbenzene (0.6 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 50/1) as an eluent, to yield the white solid **3ae** (62.0 mg, 92%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 4.5 Hz, 1H), 7.91 (d, *J* = 7.4 Hz, 2H), 7.57 (td, *J* = 7.7, 1.9 Hz, 1H) , 7.53 (t, *J* = 8.2 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.35 (dd, *J* = 8.6, 5.4 Hz, 2H), 7.14 (t, *J* = 6.1 Hz, 2H), 6.98 (t, *J* = 8.7 Hz, 2H), 4.39 (dd, *J* = 8.5, 7.1 Hz, 1H), 3.94 (dd, *J* = 13.3, 8.8 Hz, 1H), 3.78 (dd, *J* = 13.3, 6.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 161.9 (d, $^1J_{C-F}$ = 245.5 Hz), 161.2, 149.4, 138.2 (d, $^4J_{C-F}$ = 3.0 Hz), 137.0, 136.6, 133.4, 129.7 (d, $^3J_{C-F}$ = 8.0 Hz), 128.6, 127.2, 123.7, 121.9, 115.4 (d, $^2J_{C-F}$ = 21.3 Hz), 52.2, 33.9.

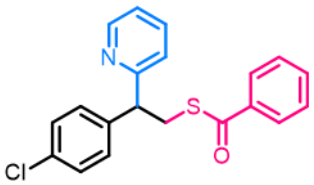
^{19}F NMR (376 MHz, $CDCl_3$) δ -115.77.

IR (KBr disc, cm^{-1}): 3846, 2924, 2355, 1659, 1590, 1506, 1462, 1431, 1302, 1213, 1163, 1091, 913, 833, 759, 687, 645, 537.

m.p.: 73.5-74.8 ℃.

QTOF-MS: *m/z* $[M + Na]^+$ Calcd for $C_{20}H_{16}FNNaOS^+$ 360.0829; Found 360.0809.

***S*-(2-(4-chlorophenyl)-2-(pyridin-2-yl)ethyl) benzothioate (3af)**



Following the General Procedure with the corresponding *S*-(pyridin-2-yl) benzothioate (0.2 mmol) and 1-chloro-4-vinylbenzene (0.6 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 50/1) as an eluent, to yield the white solid **3af** (61.4 mg, 87%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (dd, *J* = 5.2, 1.8 Hz, 1H), 7.91 (dd, *J* = 7.3, 1.2 Hz, 2H), 7.57 (td, *J* = 7.7, 1.9 Hz, 1H), 7.53 (t, *J* = 8.2 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.29 (dd, *J* = 24.0, 8.6 Hz, 4H), 7.14 (dd, *J* = 7.7, 3.5 Hz, 2H), 4.37 (dd, *J* = 8.4, 7.1 Hz, 1H), 3.93 (dd, *J* = 13.4, 8.7 Hz, 1H), 3.77 (dd, *J* = 13.4, 6.9 Hz, 1H).

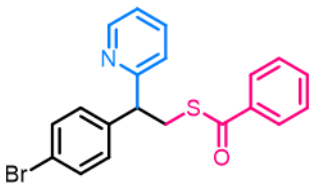
^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 161.0, 149.4, 140.9, 137.0, 136.6, 133.4, 132.9, 129.5, 128.8, 128.6, 127.2, 123.7, 122.0, 52.3, 33.7.

IR (KBr disc, cm^{-1}): 3851, 3738, 3614, 3492, 3059, 2926, 2359, 1656, 1581, 1480, 1434, 1403, 1301, 1203, 1173, 1088, 1006, 911, 824, 756, 684, 644, 530.

m.p.: 71.5-73.0 ℃.

QTOF-MS: *m/z* $[M + H]^+$ Calcd for $C_{20}H_{17}ClNOS^+$ 354.0714; Found 354.0684.

***S*-(2-(4-bromophenyl)-2-(pyridin-2-yl)ethyl) benzothioate (3ag)**



Following the General Procedure with the corresponding *S*-(pyridin-2-yl) benzothioate (0.2 mmol) and 1-bromo-4-vinylbenzene (0.6 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 50/1) as an eluent, to yield the white solid **3ag** (63.5 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (dd, *J* = 5.7, 1.7 Hz, 1H), 7.91 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.57 (td, *J* = 7.7, 1.8 Hz, 1H), 7.53 (t, *J* = 8.2 Hz, 1H), 7.44–7.37 (m, 4H), 7.29–7.24 (m, 2H), 7.15 (td,

J = 3.7, 1.1 Hz, 1H), 7.14 (d, *J* = 7.7 Hz, 1H), 4.36 (dd, *J* = 8.5, 7.0 Hz, 1H), 3.93 (dd, *J* = 13.4, 8.7 Hz, 1H), 3.77 (dd, *J* = 13.4, 6.9 Hz, 1H).

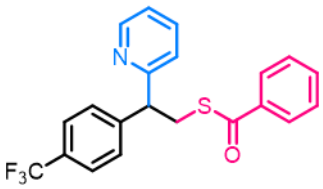
^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 160.9, 149.4, 141.4, 137.0, 136.6, 133.4, 131.7, 129.9, 128.6, 127.2, 123.7, 122.0, 121.0, 52.4, 33.6.

IR (KBr disc, cm^{-1}): 3060, 3013, 2930, 1659, 1583, 1478, 1437, 1402, 1301, 1205, 1068, 1003, 912, 823, 756, 684, 644, 614, 528, 487.

m.p.: 70.0-70.7 ℃.

QTOF-MS: *m/z* $[M + H]^+$ Calcd for $C_{20}H_{17}BrNOS^+$ 398.0209; Found 398.0201.

_S_-(2-(pyridin-2-yl)-2-(4-(trifluoromethyl)phenyl)ethyl) benzothioate (3ah)



Following the General Procedure with the corresponding *S*-(pyridin-2-yl) benzothioate (0.2 mmol) and 1-(trifluoromethyl)-4-vinylbenzene (0.6 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 50/1) as an eluent, to yield the pale yellow oil **3ah** (72.2 mg, 93%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (dd, *J* = 5.2, 1.5 Hz, 1H), 7.92 (d, *J* = 7.8 Hz, 2H), 7.63–7.49 (m, 6H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.17 (d, *J* = 7.7 Hz, 1H), 7.16 (d, *J* = 7.4 Hz, 1H), 4.50–4.42 (m, 1H), 3.97 (dd, *J* = 13.4, 8.7 Hz, 1H), 3.81 (dd, *J* = 13.4, 6.8 Hz, 1H).

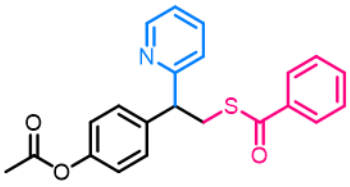
^{13}C NMR (101 MHz, $CDCl_3$) δ 191.9, 160.5, 149.5, 146.3, 136.9, 136.7, 133.5, 129.2 (q, $^{2}J_{C\text{-}F}$ = 32.4 Hz), 128.6, 128.5, 127.2, 125.6 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 124.2 (q, $^{1}J_{C\text{-}F}$ = 272.0 Hz), 123.8, 122.2, 52.8, 33.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.43.

IR (KBr disc, cm^{-1}): 3745, 3672, 2969, 2929, 2361, 1661, 1618, 1586, 1417, 1325, 1207, 1166, 1123, 1068, 1019, 909, 838, 772, 750, 689, 649.

QTOF-MS: *m/z* $[M + H]^+$ Calcd for $C_{21}H_{17}F_3NOS^+$ 388.0977; Found 388.0986.

4-(2-(benzoylthio)-1-(pyridin-2-yl)ethyl)phenyl acetate (3ai)



Following the General Procedure with the corresponding *S*-(pyridin-2-yl) benzothioate (0.2 mmol) and 4-vinylphenyl acetate (0.6 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 50/1) as an eluent, to yield the white solid **3ai** (55.8 mg, 74%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 4.4 Hz, 1H), 7.91 (dd, *J* = 7.2, 1.4 Hz, 2H), 7.56 (td, *J* = 7.6, 1.7 Hz, 1H), 7.53 (t, *J* = 8.2 Hz, 1H), 7.44–7.35 (m, 4H), 7.18–7.10 (m, 2H), 7.05–6.99 (m,

2H), 4.40 (dd, *J* = 9.0, 6.6 Hz, 1H), 3.94 (dt, *J* = 14.0, 7.0 Hz, 1H), 3.79 (dd, *J* = 13.3, 6.5 Hz, 1H), 2.27 (s, 3H).

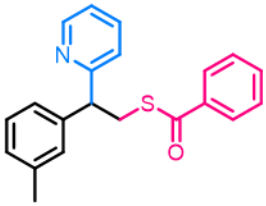
^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 169.5, 161.1, 149.6, 149.3, 140.0, 137.0, 136.6, 133.3, 129.1, 128.6, 127.2, 123.9, 121.9, 121.6, 52.4, 33.8, 21.2.

IR (KBr disc, cm^{-1}): 3005, 2928, 1982, 1924, 1748, 1655, 1586, 1505, 1467, 1431, 1366, 1309, 1281, 1200, 1171, 1103, 1046, 1017, 906, 874, 837, 812, 789, 754, 717, 685, 640.

m.p.: 91.0-92.5 ℃.

QTOF-MS: *m/z* $[M + H]^+$ Calcd for $C_{22}H_{20}NO_3S^+$ 378.1158; Found 378.1155.

_S_-(2-(pyridin-2-yl)-2-(_m_-tolyl)ethyl) benzothioate (3aj)



Following the General Procedure with the corresponding *S*-(pyridin-2-yl) benzothioate (0.2 mmol) and 1-methyl-3-vinylbenzene (0.6 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 50/1) as an eluent, to yield the white solid **3aj** (60.6 mg, 91%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (dd, *J* = 4.8, 0.8 Hz, 1H), 7.91 (dd, *J* = 7.2, 1.4 Hz, 2H), 7.54 (td, *J* = 7.7, 1.8 Hz, 1H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.38 (dd, *J* = 10.7, 4.8 Hz, 2H), 7.22–7.14 (m, 4H), 7.12 (ddd, *J* = 7.4, 4.9, 1.0 Hz, 1H), 7.03 (d, *J* = 7.1 Hz, 1H), 4.37 (dd, *J* = 9.0, 6.7 Hz, 1H), 3.97 (dd, *J* = 13.3, 9.0 Hz, 1H), 3.81 (dd, *J* = 13.3, 6.6 Hz, 1H), 2.31 (s, 3H).

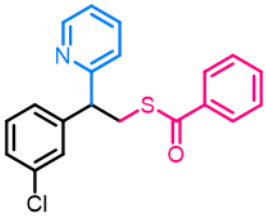
^{13}C NMR (101 MHz, $CDCl_3$) δ 192.1, 161.6, 149.2, 142.4, 138.3, 137.1, 136.5, 133.3, 128.8, 128.6, 127.84, 127.26, 125.08, 123.76, 121.77, 52.94, 33.70, 21.51.

IR (KBr disc, cm^{-1}): 3869, 3856, 3829, 3744, 3054, 3015, 2924, 2358, 1656, 1579, 1462, 1432, 1203, 1172, 1088, 1042, 908, 758, 685, 642.

m.p.: 55.1-56.2 ℃.

QTOF-MS: *m/z* $[M + H]^+$ Calcd for $C_{21}H_{20}NOS^+$ 334.1260; Found 334.1239.

_S_-(2-(3-chlorophenyl)-2-(pyridin-2-yl)ethyl) benzothioate (3ak)



Following the General Procedure with the corresponding *S*-(pyridin-2-yl) benzothioate (0.2 mmol) and 1-chloro-3-vinylbenzene (0.6 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 50/1) as an eluent, to yield the transparent oil **3ak** (48.7 mg, 69%).

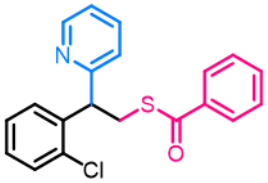
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (dd, *J* = 5.4, 1.8 Hz, 1H), 7.91 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.57 (td, *J* = 7.7, 1.8 Hz, 1H), 7.52 (ddd, *J* = 7.0, 4.1, 1.3 Hz, 1H), 7.43–7.36 (m, 3H), 7.28 (dt, *J* = 7.3, 1.6 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.20 (t, *J* = 1.8 Hz, 1H), 7.17–7.12 (m, 2H), 4.37 (dd, *J* = 8.8, 6.7 Hz, 1H), 3.94 (dd, *J* = 13.4, 8.9 Hz, 1H), 3.78 (dd, *J* = 13.3, 6.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.9, 160.7, 149.5, 144.4, 137.0, 136.6, 134.4, 133.4, 129.9, 128.6, 128.3, 127.3, 126.4, 123.8, 122.1, 52.6, 33.7.

IR (KBr disc, cm^{-1}): 3594, 2975, 2361, 1924, 1661, 1382, 1048, 881, 690.

QTOF-MS: *m/z* $[M + H]^+$ Calcd for $C_{20}H_{17}ClNOS^+$ 354.0714; Found 354.0693.

S-(2-(2-chlorophenyl)-2-(pyridin-2-yl)ethyl) benzothioate (3al)



Following the General Procedure with the corresponding *S*-(pyridin-2-yl) benzothioate (0.2 mmol) and 1-chloro-3-vinylbenzene (0.6 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 50/1) as an eluent, to yield the white solid **3al** (59.3 mg, 84%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 4.7 Hz, 1H), 7.90 (d, *J* = 7.6 Hz, 2H), 7.55 (d, *J* = 1.6 Hz, 1H), 7.50 (dd, *J* = 16.1, 8.1 Hz, 2H), 7.41–7.33 (m, 3H), 7.20 (t, *J* = 6.9 Hz, 2H), 7.17–7.09 (m, 2H), 5.03 (t, *J* = 7.8 Hz, 1H), 3.99 (dd, *J* = 13.2, 8.3 Hz, 1H), 3.84 (dd, *J* = 13.2, 7.3 Hz, 1H).

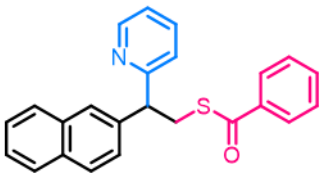
^{13}C NMR (101 MHz, $CDCl_3$) δ 191.7, 160.6, 149.4, 139.7, 137.1, 136.5, 134.1, 133.3, 129.7, 129.3, 128.5, 128.2, 127.3, 127.1, 124.0, 122.0, 48.1, 32.9.

IR (KBr disc, cm^{-1}): 3061, 2924, 2853, 1958, 1686, 1657, 1614, 1585, 1487, 1449, 1394, 1333, 1287, 1226, 1204, 1173, 1125, 1095, 1053, 1031, 997, 927, 908, 862, 814, 752, 685, 647, 623.

m.p.: 50.1-51.2 ℃.

QTOF-MS: *m/z* $[M + H]^+$ Calcd for $C_{20}H_{17}ClNOS^+$ 354.0714; Found 354.0696.

S-(2-(naphthalen-2-yl)-2-(pyridin-2-yl)ethyl) benzothioate (3am)



Following the General Procedure with the corresponding *S*-(pyridin-2-yl) benzothioate (0.2 mmol) and 2-vinylnaphthalene (0.6 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 50/1) as an eluent, to yield the white solid **3am** (33.2 mg, 45%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (dd, *J* = 4.8, 0.8 Hz, 1H), 7.92 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.80 (dd, *J* = 9.9, 5.0 Hz, 4H), 7.56 (td, *J* =7.7, 1.8 Hz, 1H), 7.52 (ddd, *J* = 7.7, 4.9, 1.0 Hz, 2H), 7.59–

7.49 (m, 3H), 7.48–7.36 (m, 4H), 7.20 (d, *J* = 7.9 Hz, 1H), 7.14 (ddd, *J* = 7.4, 4.9, 1.0 Hz, 1H), 4.58 (dd, *J* = 8.5, 7.1 Hz, 1H), 4.07 (dd, *J* = 13.3, 8.7 Hz, 1H), 3.91 (dd, *J* = 13.3, 6.9 Hz, 1H).

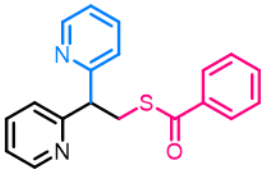
^{13}C NMR (101 MHz, $CDCl_3$) δ 192.1, 161.4, 149.3, 139.9, 137.1, 136.5, 133.5, 133.3, 132.5, 128.6, 128.4, 127.9, 127.6, 127.3, 126.8, 126.3, 126.1, 125.8, 123.9, 121.9, 53.1, 33.6.

IR (KBr disc, cm^{-1}): 3056, 3006, 2940, 2851, 2361, 1643, 1579, 1568, 1506, 1487, 1471, 1432, 1412, 1204, 1160, 911, 861, 808, 685, 478, 458, 431, 413, 403.

m.p.: 81.0-82.5 ℃.

QTOF-MS: *m/z* $[M + H]^+$ Calcd for $C_{24}H_{20}NOS^+$ 370.1260; Found 370.1235.

***S*-(2,2-di(pyridin-2-yl)ethyl) benzothioate (3an)**



Following the General Procedure with the corresponding *S*-(pyridin-2-yl) benzothioate (0.2 mmol) and 2-vinylpyridine (0.6 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 50/1) as an eluent, to yield the white solid **3an** (44.2 mg, 69%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (dd, *J* = 4.8, 0.8 Hz, 2H), 7.96–7.86 (m, 2H), 7.60 (td, *J* = 7.7, 1.8 Hz, 2H), 7.53 (dd, *J* = 10.5, 4.3 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.34 (d, *J* = 7.8 Hz, 2H), 7.14 (ddd, *J* = 7.4, 4.9, 0.8 Hz, 2H), 4.62 (t, *J* = 7.8 Hz, 1H), 4.01 (d, *J* = 7.8 Hz, 2H).

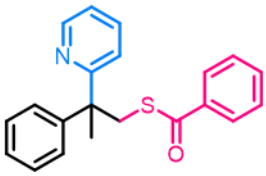
^{13}C NMR (101 MHz, $CDCl_3$) δ 191.8, 160.8, 149.4, 137.1, 136.6, 133.3, 128.5, 127.3, 123.4, 122.0, 55.1, 32.6.

IR (KBr disc, cm^{-1}): 3050, 3035, 3009, 2920, 2850, 2360, 1656, 1583, 1567, 1467, 1448, 1432, 1395, 1201, 1177, 1152, 1096, 1074, 1052, 905, 769, 749, 683, 628, 614, 595, 532, 414, 403.

m.p.: 70.1-71.8 ℃.

QTOF-MS: *m/z* $[M + H]^+$ Calcd for $C_{19}H_{17}N_2OS^+$ 321.1056; Found 321.1064.

***S*-(2-phenyl-2-(pyridin-2-yl)propyl) benzothioate (3ao)**



Following the General Procedure with the corresponding *S*-(pyridin-2-yl) benzothioate (0.2 mmol) and prop-1-en-2-ylbenzene (0.6 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 50/1) as an eluent, to yield the white solid **3ao** (40.0 mg, 60%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 4.1 Hz, 1H), 7.95–7.88 (m, 2H), 7.55 (td, *J* = 7.8, 1.8 Hz, 1H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.32–7.24 (m, 5H), 7.23–7.17 (m, 1H), 7.15–7.08 (m, 2H), 4.12 (d, *J* = 13.2 Hz, 1H), 4.00 (d, *J* = 13.2 Hz, 1H), 1.84 (s, 3H).

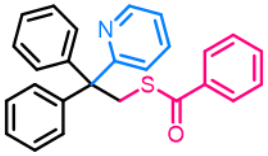
^{13}C NMR (101 MHz, $CDCl_3$) δ 192.1, 166.1, 148.3, 146.8, 137.3, 136.3, 133.1, 128.5, 128.3, 127.3, 127.1, 126.6, 122.4, 121.4, 49.5, 40.1, 25.4.

IR (KBr disc, cm^{-1}): 3054, 3002, 2974, 2924, 1961, 1652, 1586, 1565, 1493, 1467, 1444, 1427, 1376, 1291, 1261, 1201, 1173, 1156, 1134, 1091, 1064, 1026, 995, 969, 910, 844, 812, 792, 767, 734, 684, 646, 618.

m.p.: 88.6-90.1 ℃.

QTOF-MS: *m/z* $[M + H]^+$ Calcd for $C_{21}H_{20}NOS^+$ 334.1260; Found 334.1250.

***S*-(2,2-diphenyl-2-(pyridin-2-yl)ethyl) benzothioate (3ap)**



Following the General Procedure with the corresponding *S*-(pyridin-2-yl) benzothioate (0.2 mmol) and ethene-1,1-diyldibenzene (0.6 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 50/1) as an eluent, to yield the white solid **3ap** (64.8 mg, 82%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (dd, *J* = 5.4, 1.8 Hz, 1H), 7.82–7.75 (m, 2H), 7.52 (td, *J* = 7.7, 1.9 Hz, 1H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.31 (t, *J* = 7.7 Hz, 2H), 7.28–7.16 (m, 10H), 7.11 (dd, *J* = 7.6, 4.0 Hz, 2H), 4.52 (s, 2H).

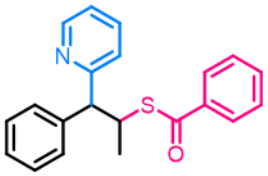
^{13}C NMR (101 MHz, $CDCl_3$) δ 192.2, 164.8, 148.5, 145.2, 137.4, 135.9, 132.9, 129.3, 128.4, 128.0, 127.2, 126.8, 124.8, 121.5, 59.8, 39.6.

IR (KBr disc, cm^{-1}): 3055, 3029, 2921, 2849, 1964, 1635, 1586, 1488, 1467, 1444, 1429, 1294, 1262, 1207, 1178, 1153, 1099, 1034, 997, 965, 931, 916, 844, 812, 791, 773, 750, 697, 688, 650, 637, 614.

m.p.: 155.5-156.6 ℃.

QTOF-MS: *m/z* $[M + H]^+$ Calcd for $C_{26}H_{22}NOS^+$ 396.1417; Found 396.1401.

***S*-(1-phenyl-1-(pyridin-2-yl)propan-2-yl) benzothioate (3aq)**



Following the General Procedure with the corresponding *S*-(pyridin-2-yl) benzothioate (0.2 mmol) and 1-propenylbenzene (0.6 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 50/1) as an eluent, to yield the white solid **3aq** (49.3 mg, 74%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (dd, *J* = 4.8, 0.9 Hz, 1H), 7.85 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.51 (td, *J* = 7.7, 1.7 Hz, 1H), 7.48 (dd, *J* = 7.2, 6.0 Hz, 3H), 7.36 (dd, *J* = 10.6, 4.8 Hz, 2H), 7.30 (dd, *J* = 10.3, 4.7 Hz, 2H), 7.25 (d, *J* = 7.9 Hz, 1H), 7.23–7.17 (m, 1H), 7.04 (ddd, *J* = 7.5, 4.9, 1.0 Hz, 1H), 4.80 (dq, *J* = 10.6, 6.8 Hz, 1H), 4.32 (d, *J* = 10.6 Hz, 1H), 1.39 (d, *J* = 6.8 Hz, 3H).

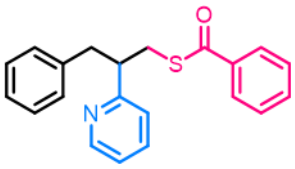
^{13}C NMR (101 MHz, $CDCl_3$) δ 191.6, 161.6, 149.3, 141.2, 137.3, 136.4, 133.1, 128.6, 128.6, 128.5, 127.2, 127.1, 123.0, 121.7, 58.6, 43.2, 21.0.

IR (KBr disc, cm^{-1}): 3284, 3077, 3052, 3023, 2962, 2923, 2864, 1646, 1586, 1490, 1470, 1450, 1432, 1373, 1348, 1312, 1298, 1261, 1206, 1152, 1117, 1070, 1019, 994, 909, 771, 748, 688, 649, 618.

m.p.: 112.7-113.8 ℃.

QTOF-MS: *m/z* $[M + H]^+$ Calcd for $C_{21}H_{20}NOS^+$ 334.1260; Found 334.1261.

_S_-(3-phenyl-2-(pyridin-2-yl)propyl) benzothioate (3ar)



Following the General Procedure with the corresponding *S*-(pyridin-2-yl) benzothioate (0.2 mmol) and allylbenzene (0.6 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 50/1) as an eluent, to yield the transparent oil **3ar** (37.3 mg, 56%).

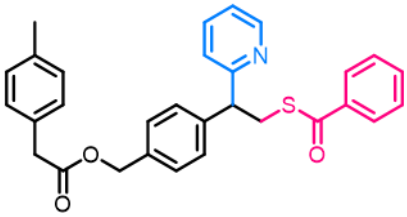
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (dd, *J* = 4.8, 0.9 Hz, 1H), 7.91 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.54 (ddd, *J* = 8.5, 2.4, 1.1 Hz, 1H), 7.47 (td, *J* = 7.6, 1.8 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.21–7.09 (m, 4H), 7.02 (d, *J* = 6.7 Hz, 2H), 6.87 (d, *J* = 7.8 Hz, 1H), 3.54 (ddd, *J* = 21.8, 13.2, 7.3 Hz, 2H), 3.35 (tt, *J* = 8.5, 6.2 Hz, 1H), 3.21–3.09 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.8, 161.7, 149.5, 139.5, 137.1, 136.1, 133.3, 129.1, 128.6, 128.2, 127.23, 126.1, 124.1, 121.8, 49.4, 41.5, 33.5.

IR (KBr disc, cm^{-1}): 3280, 3022, 2961, 2923, 2361, 1658, 1577, 1572, 1492, 1471, 1432, 1202, 1172, 1161, 1148, 1076, 1012, 910, 836, 800, 774, 758, 688, 496, 477, 469.

QTOF-MS: *m/z* $[M + H]^+$ Calcd for $C_{21}H_{19}NNaOS^+$ 356.1080; Found 356.1088.

4-(2-(benzoylthio)-1-(pyridin-2-yl)ethyl)benzyl 2-(*p*-tolyl)acetate (3as)



Following the General Procedure with the corresponding *S*-(pyridin-2-yl) benzothioate (0.2 mmol) and 4-vinylbenzyl 2-(*p*-tolyl)acetate (0.6 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 50/1) as an eluent, to yield the transparent oil **3as** (63.5 mg, 66%).

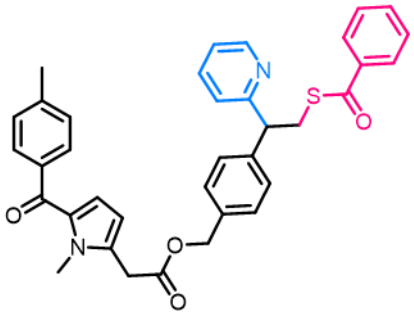
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (dd, *J* = 4.8, 0.8 Hz, 1H), 7.91 (dd, *J* = 8.2, 1.1 Hz, 2H), 7.60–7.53 (m, 1H), 7.51 (d, *J* = 7.4 Hz, 1H), 7.42–7.34 (m, 4H), 7.25 (d, *J* = 8.2 Hz, 2H), 7.13 (dd, *J* = 18.5, 8.0 Hz, 6H), 5.07 (s, 2H), 4.41 (dd, *J* = 8.8, 6.8 Hz, 1H), 3.96 (dd, *J* = 13.3, 8.8 Hz, 1H), 3.80 (dd, *J* = 13.3, 6.7 Hz, 1H), 3.60 (s, 2H), 2.31 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 171.7, 161.2, 149.3, 142.5, 137.1, 136.8, 136.6, 134.6, 133.4, 130.8, 129.3, 129.2, 128.6, 128.5, 128.3, 127.3, 123.8, 121.9, 66.3, 52.7, 40.9, 33.7, 21.1.

IR (KBr disc, cm^{-1}): 3052, 2952, 2924, 1733, 1658, 1616, 1589, 1581, 1569, 1515, 1471, 1448, 1433, 1206, 1146, 909, 773, 750, 688, 648, 616, 442, 414, 403.

QTOF-MS: *m/z* $[M + H]^+$ Calcd for $C_{30}H_{28}NO_3S^+$ 482.1784; Found 482.1784.

4-(2-(benzoylthio)-1-(pyridin-2-yl)ethyl)benzyl 2-(1-methyl-5-(4-methylbenzoyl)-1H-pyrrol-2-yl)acetate (3at)



Following the General Procedure with the corresponding *S*-(pyridin-2-yl) benzothioate (0.2 mmol) and 4-vinylbenzyl 2-(1-methyl-5-(4-methylbenzoyl)-1H-pyrrol-2-yl)acetate (0.6 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 50/1) as an eluent, to yield the transparent oil **3at** (72.9 mg, 62%).

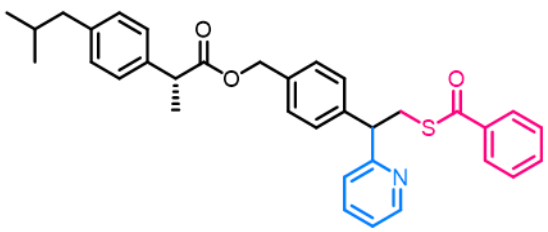
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (dd, *J* = 4.8, 0.8 Hz, 1H), 7.91 (dd, *J* = 5.2, 3.3 Hz, 2H), 7.70 (d, *J* = 8.1 Hz, 2H), 7.56 (td, *J* = 8.1, 1.8 Hz, 1H), 7.52(t, *J* = 7.4 Hz, 1H), 7.44–7.36 (m, 4H), 7.28 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 7.13 (ddd, *J* = 8.2, 5.9, 4.4 Hz, 2H), 6.66 (d, *J* = 4.0 Hz, 1H), 6.09 (d, *J* = 4.1 Hz, 1H), 5.13 (s, 2H), 4.41 (dd, *J* = 8.7, 6.8 Hz, 1H), 3.96 (dd, *J* = 13.3, 8.8 Hz, 1H), 3.90 (s, 3H), 3.80 (dd, *J* = 13.3, 6.7 Hz, 1H), 3.72 (s, 2H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 185.9, 169.2, 161.2, 149.4, 142.8, 141.9, 137.4, 137.1, 136.6, 134.3, 134.1, 133.4, 131.5, 129.5, 128.7, 128.7, 128.6, 128.4, 127.2, 123.8, 122.3, 121.9, 109.5, 66.9, 52.7, 33.7, 33.2, 32.9, 21.6.

IR (KBr disc, cm^{-1}): 2951, 1736, 1657, 1621, 1605, 1568, 1512, 1481, 1454, 1433, 1407, 1373, 1263, 1204, 1172, 1112, 1043, 995, 979, 882, 834, 773, 748, 688, 648, 617, 415, 404.

QTOF-MS: *m/z* $[M + H]^+$ Calcd for $C_{36}H_{33}N_2O_4S^+$ 589.2156; Found 589.2156.

4-(2-(benzoylthio)-1-(pyridin-2-yl)ethyl)benzyl (2*R*)-2-(4-isobutylphenyl)propanoate (3au)



Following the General Procedure with the corresponding *S*-(pyridin-2-yl) benzothioate (0.2 mmol) and 4-vinylbenzyl (*R*)-2-(4-isobutylphenyl)propanoate (0.6 mmol). The crude product was purified

by preparative TLC, using PE and EA (v/v = 50/1) as an eluent, to yield the transparent oil **3au** (77.3 mg, 72%).

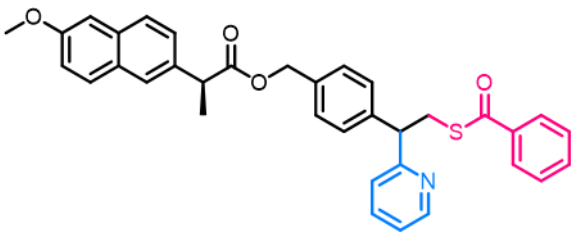
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (dd, *J* = 5.8, 1.5 Hz, 1H), 7.91 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.60–7.50 (m, 2H), 7.40 (dd, *J* = 10.8, 4.7 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.16 (tt, *J* = 7.5, 3.1 Hz, 6H), 7.07 (dd, *J* = 8.1, 1.9 Hz, 2H), 5.06 (q, *J* = 12.6 Hz, 2H), 4.39 (dd, *J* = 8.7, 6.8 Hz, 1H), 3.95 (dd, *J* = 13.3, 8.9 Hz, 1H), 3.78 (dd, *J* = 13.3, 6.7 Hz, 1H), 3.73 (q, *J* = 7.2 Hz, 1H), 2.44 (d, *J* = 7.2 Hz, 2H), 1.84 (tp, *J* = 13.1, 6.6 Hz, 1H), 1.49 (d, *J* = 7.2 Hz, 3H), 0.89 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 174.6, 161.3, 149.3, 142.3, 140.6, 137.6, 137.1, 136.6, 134.8, 133.3, 129.3, 128.6, 128.2, 128.1, 127.2, 127.2, 123.8, 121.9, 66.0, 52.7, 45.1, 45.0, 33.7, 30.2, 22.4, 18.5.

IR (KBr disc, cm^{-1}): 2954, 2931, 2868, 2350, 1733, 1659, 1589, 1570, 1513, 1448, 1434, 1380, 1205, 1092, 1074, 1021, 1009, 997, 909, 847, 773, 749, 689, 649, 616, 597, 540, 422.

QTOF-MS: *m/z* $[M + H]^+$ Calcd for $C_{34}H_{36}NO_3S^+$ 538.2410; Found 538.2410.

4-(2-(benzoylthio)-1-(pyridin-2-yl)ethyl)benzyl (2*S*)-2-(6-methoxynaphthalen-2-yl)propanoate (3av)



Following the General Procedure with the corresponding *S*-(pyridin-2-yl) benzothioate (0.2 mmol) and 4-vinylbenzyl (*S*)-2-(6-methoxynaphthalen-2-yl)propanoate (0.6 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 50/1) as an eluent, to yield the transparent oil **3av** (62.8 mg, 56%).

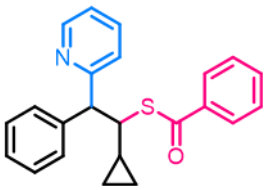
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (dd, *J* = 5.6, 1.7 Hz, 1H), 7.90 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.70–7.60 (m, 3H), 7.56–7.47 (m, 2H), 7.41–7.34 (m, 3H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 7.14–7.07 (m, 4H), 5.06 (dd, *J* = 28.5, 12.5 Hz, 2H), 4.38 (dd, *J* = 8.8, 6.7 Hz, 1H), 3.98–3.91 (m, 1H), 3.90–3.83 (m, 4H), 3.77 (dd, *J* = 13.3, 6.7 Hz, 1H), 1.57 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.9, 173.4, 160.2, 156.6, 148.2, 141.3, 136.0, 135.5, 134.5, 133.7, 132.6, 132.3, 128.2, 127.9, 127.5, 127.2, 127.2, 126.2, 126.1, 125.2, 124.9, 122.7, 120.8, 117.9, 104.6, 65.1, 54.2, 51.6, 44.4, 32.6, 17.5.

IR (KBr disc, cm^{-1}): 3060, 2966, 2936, 1726, 1667, 1651, 1604, 1581, 1513, 1448, 1434, 1393, 1329, 1262, 1197, 1177, 1090, 1028, 909, 854, 818, 746, 684, 458, 443, 420.

QTOF-MS: *m/z* $[M + H]^+$ Calcd for $C_{35}H_{32}NO_4S^+$ 562.2047; Found 562.2047.

***S*-(1-cyclopropyl-2-phenyl-2-(pyridin-2-yl)ethyl) benzothioate (3aw)**



Following the General Procedure with the corresponding *S*-(pyridin-2-yl) benzothioate (0.2 mmol) and (*E*)/(*Z*)-(2-cyclopropylvinyl)benzene (0.6 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 50/1) as an eluent, to yield the white solid **3aw** (58.2 mg, 81%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (dd, *J* = 4.8, 0.8 Hz, 1H), 7.90–7.81 (m, 2H), 7.56 – 7.39 (m, 4H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.25 (dd, *J* = 14.2, 6.9 Hz, 3H), 7.18 (dd, *J* = 8.3, 6.3 Hz, 1H), 7.08–7.02 (m, 1H), 4.64 (d, *J* = 9.4 Hz, 1H), 4.28 (t, *J* = 9.3 Hz, 1H), 1.21–1.08 (m, 1H), 0.44–0.30 (m, 3H), 0.20 (ddd, *J* = 12.6, 6.0, 2.9 Hz, 1H).

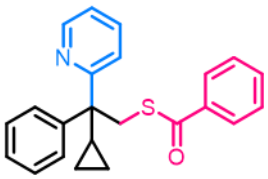
^{13}C NMR (101 MHz, $CDCl_3$) δ 191.8, 161.6, 149.1, 141.6, 137.3, 136.3, 133.1, 129.0, 128.4, 128.3, 127.3, 126.8, 123.4, 121.7, 58.4, 52.9, 16.6, 8.2, 3.7.

IR (KBr disc, cm^{-1}): 3077, 3021, 2922, 1652, 1581, 1491, 1473, 1455, 1433, 1347, 1206, 1179, 1163, 1076, 1024, 910, 824, 772, 726, 691, 648, 603, 574, 442, 413.

m.p.: 101.3-103.0 ℃.

QTOF-MS: *m/z* $[M + H]^+$ Calcd for $C_{23}H_{22}NOS^+$ 360.1417; Found 360.1410.

S-(2-cyclopropyl-2-phenyl-2-(pyridin-2-yl)ethyl) benzothioate (3ax)



Following the General Procedure with the corresponding *S*-(pyridin-2-yl) benzothioate (0.2 mmol) and (1-cyclopropylvinyl)benzene (0.6 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 50/1) as an eluent, to yield the transparent oil **3ax** (53.9 mg, 75%).

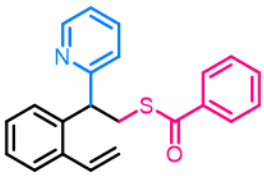
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (dd, *J* = 4.8, 1.0 Hz, 1H), δ 7.88 (dd, *J* = 7.2, 1.3 Hz, 2H), 7.56 (td, *J* = 7.8, 1.9 Hz, 1H), 7.52–7.46 (m, 1H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.26 (q, *J* = 1.8 Hz, 4H), 7.20 (ddd, *J* = 12.9, 8.2, 5.3 Hz, 2H), 7.13 (ddd, *J* = 7.4, 4.8, 0.9 Hz, 1H), 4.24 (dd, *J* = 51.2, 12.8 Hz, 2H), 1.69 (tt, *J* = 8.4, 5.7 Hz, 1H), 0.59–0.52 (m, 2H), 0.08 (ddd, *J* = 7.0, 4.7, 2.4 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 189.7, 162.0, 146.4, 141.9, 135.2, 133.3, 130.9, 126.6, 126.3, 125.7, 125.1, 124.5, 122.1, 119.3, 50.8, 37.6, 16.2, 0.0, -0.4.

IR (KBr disc, cm^{-1}): 3078, 3018, 2920, 1657, 1581, 1490, 1475, 1445, 1432, 1348, 1216, 1189, 1162, 1077, 1023, 912, 826, 777, 723, 648, 606, 442, 412.

QTOF-MS: *m/z* $[M + H]^+$ Calcd for $C_{23}H_{21}NNaOS^+$ 382.1236; Found 382.1232.

S-(2-(pyridin-2-yl)-2-(2-vinylphenyl)ethyl) benzothioate (3ay)



Following the General Procedure with the corresponding *S*-(pyridin-2-yl) benzothioate (0.2 mmol) and 1,2-divinylbenzene (0.6 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 50/1) as an eluent, to yield the white solid **3ay** (50.4 mg, 73%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 4.2 Hz, 1H), 7.91 (d, *J* = 8.3 Hz, 2H), 7.58–7.47 (m, 2H), 7.39 (dd, *J* = 13.3, 5.1 Hz, 3H), 7.32–7.25 (m, 2H), 7.22–7.09 (m, 3H), 6.68 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.73 (d, *J* = 17.6 Hz, 1H), 5.22 (d, *J* = 10.9 Hz, 1H), 4.41 (dd, *J* = 8.6, 7.0 Hz, 1H), 3.98 (dd, *J* = 13.1, 8.9 Hz, 1H), 3.82 (dd, *J* = 13.2, 6.6 Hz, 1H).

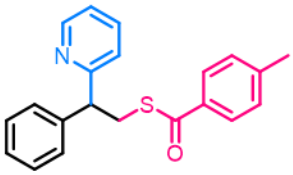
^{13}C NMR (101 MHz, $CDCl_3$) δ 192.1, 161.3, 149.3, 142.7, 137.9, 137.1, 136.8, 136.5, 133.3, 128.9, 128.6, 127.6, 127.3, 126.2, 124.8, 123.8, 121.9, 114.1, 52.9, 33.7.

IR (KBr disc, cm^{-1}): 3057, 3006, 2965, 2931, 2350, 1657, 1589, 1581, 1488, 1471, 1432, 1292, 1205, 1175, 1095, 995, 910, 803, 773, 747, 714, 688, 648, 417, 405.

m.p.: 88.2-89.2 ℃.

QTOF-MS: *m/z* $[M + H]^+$ Calcd for $C_{22}H_{20}NOS^+$ 346.1260; Found 346.1263.

_S_-(2-phenyl-2-(pyridin-2-yl)ethyl) 4-methylbenzothioate (3ba)



Following the General Procedure with the corresponding *S*-(pyridin-2-yl) 4-methylbenzothioate (0.2 mmol) and styrene (0.6 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 50/1) as an eluent, to yield the white solid **3ba** (53.3 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (ddd, *J* = 4.8, 1.7, 0.8 Hz, 1H), 7.84–7.78 (m, 2H), 7.56 (td, *J* = 7.7, 1.8 Hz, 1H), 7.37 (dd, *J* = 8.1, 1.1 Hz, 2H), 7.33–7.27 (m, 2H), 7.23 (dt, *J* = 4.5, 1.8 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 7.9 Hz, 1H), 7.13 (ddd, *J* = 7.5, 5.0, 1.2 Hz, 1H), 4.40 (dd, *J* = 8.8, 6.8 Hz, 1H), 3.95 (dd, *J* = 13.3, 8.9 Hz, 1H), 3.80 (dd, *J* = 13.3, 6.7 Hz, 1H), 2.37 (s, 3H).

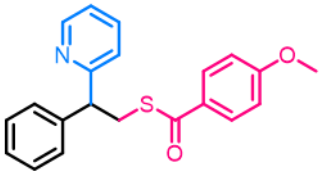
^{13}C NMR (101 MHz, $CDCl_3$) δ 191.7, 161.5, 149.3, 144.1, 142.5, 136.5, 134.6, 129.2, 128.6, 128.1, 127.3, 127.0, 123.8, 121.8, 53.0, 33.6, 21.7.

IR (KBr disc, cm^{-1}): 3027, 3001, 2923, 2854, 2361, 1950, 1913, 1700, 1642, 1603, 1585, 1493, 1469, 1452, 1430, 1405, 1307, 1270, 1205, 1170, 1148, 1113, 1076, 1036, 993, 909, 840, 814, 790, 746, 717, 697, 643, 627.

m.p.: 73.7-74.6 ℃.

QTOF-MS: *m/z* $[M + H]^+$ Calcd for $C_{21}H_{20}NOS^+$ 334.1260; Found 334.1268.

***S*-(2-phenyl-2-(pyridin-2-yl)ethyl) 4-methoxybenzothioate (3ca)**



Following the General Procedure with the corresponding *S*-(pyridin-2-yl) 4-methoxybenzothioate (0.2 mmol) and styrene (0.6 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 50/1) as an eluent, to yield the transparent oil **3ca** (60.7 mg, 87%).

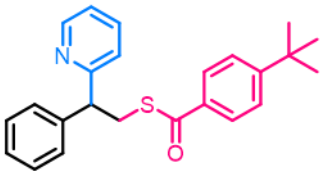
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 4.7 Hz, 1H), 7.90 (d, *J* = 8.8 Hz, 2H), 7.56 (td, *J* = 7.7, 1.6 Hz, 1H), 7.37 (d, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.24–7.19 (m, 1H), 7.18–7.11 (m, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 4.40 (dd, *J* = 8.6, 6.9 Hz, 1H), 3.95 (dd, *J* = 13.3, 8.9 Hz, 1H), 3.83 (s, 3H), 3.79 (dd, *J* = 13.3, 6.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.6, 163.7, 161.6, 149.2, 142.5, 136.5, 130.0, 129.4, 128.6, 128.1, 127.0, 123.8, 121.8, 113.7, 55.5, 53.1, 33.6.

IR (KBr disc, cm^{-1}): 3446, 2975, 2927, 2901, 2361, 2338, 1652, 1599, 1506, 1456, 1310, 1259, 1216, 1166, 1081, 1049, 911, 882, 837, 749, 697, 673, 645, 621, 526, 422.

QTOF-MS: *m/z* $[M + H]^+$ Calcd for $C_{21}H_{20}NO_2S^+$ 350.1209; Found 350.1201.

***S*-(2-phenyl-2-(pyridin-2-yl)ethyl) 4-(*tert*-butyl)benzothioate (3da)**



Following the General Procedure with the corresponding *S*-(pyridin-2-yl) 4-(*tert*-butyl)benzothioate (0.2 mmol) and styrene (0.6 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 50/1) as an eluent, to yield the white solid **3da** (57.0 mg, 76%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (dd, *J* = 4.9, 0.8 Hz, 1H), 7.91–7.81 (m, 2H), 7.55 (td, *J* = 7.7, 1.8 Hz, 1H), 7.43–7.35 (m, 4H), 7.30 (dd, *J* = 10.2, 4.8 Hz, 2H), 7.24–7.19 (m, 1H), 7.15 (d, *J* = 7.8 Hz, 1H), 7.12 (ddd, *J* = 7.4, 4.9, 1.0 Hz, 1H), 4.40 (dd, *J* = 8.8, 6.8 Hz, 1H), 3.96 (dd, *J* = 13.3, 8.9 Hz, 1H), 3.80 (dd, *J* = 13.3, 6.7 Hz, 1H), 1.30 (s, 9H).

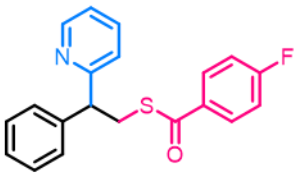
^{13}C NMR (101 MHz, $CDCl_3$) δ 191.7, 161.6, 157.1, 149.3, 142.5, 136.5, 134.5, 128.6, 128.1, 127.2, 127.0, 125.5, 123.8, 121.8, 53.0, 35.1, 33.7, 31.1.

IR (KBr disc, cm^{-1}): 2962, 2924, 2361, 2341, 1655, 1588, 1473, 1432, 1413, 1261, 1204, 1091, 1018, 908, 795, 762, 689, 649, 614, 567, 416.

m.p.: 97.1-99.3 ℃.

QTOF-MS: *m/z* $[M + H]^+$ Calcd for $C_{24}H_{26}NOS^+$ 376.1730; Found 376.1663.

***S*-(2-phenyl-2-(pyridin-2-yl)ethyl) 4-fluorobenzothioate (3ea)**



Following the General Procedure with the corresponding *S*-(pyridin-2-yl) 4-fluorobenzothioate (0.2 mmol) and styrene (0.6 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 50/1) as an eluent, to yield the white solid **3ea** (50.5 mg, 75%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (dd, *J* = 4.8, 0.8 Hz, 1H), 7.97–7.89 (m, 2H), 7.56 (td, *J* = 7.7, 1.8 Hz, 1H), 7.40–7.34 (m, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.25–7.19 (m, 1H), 7.13 (ddd, *J* = 7.9, 5.9, 4.3 Hz, 2H), 7.10–7.03 (m, 2H), 4.40 (dd, *J* = 8.9, 6.7 Hz, 1H), 3.98 (dd, *J* = 13.3, 8.9 Hz, 1H), 3.81 (dd, *J* = 13.3, 6.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.6, 165.9 (d, $^1J_{C\text{-}F}$ = 254.7 Hz), 161.4, 149.3, 142.4, 136.5, 133.5 (d, $^4J_{C\text{-}F}$ = 2.9 Hz), 129.8 (d, $^3J_{C\text{-}F}$ = 9.4 Hz), 128.7, 128.1, 127.1, 123.8, 121.8, 115.7 (d, $^2J_{C\text{-}F}$ = 22.0 Hz), 77.4, 77.1, 76.8, 52.9, 33.8.

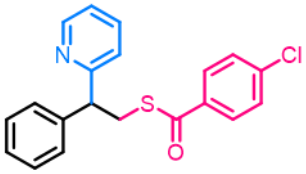
^{19}F NMR (376 MHz, $CDCl_3$) δ -104.89.

IR (KBr disc, cm^{-1}): 3299, 2976, 2930, 2898, 2410, 2361, 2337, 2257, 2133, 1922, 1658, 1596, 1500, 1432, 1408, 1297, 1204, 1155, 1085, 1048, 919, 844, 806, 750, 729, 699, 642, 620, 520, 436.

m.p.: 67.4-68.0 ℃.

QTOF-MS: *m/z* $[M + H]^+$ Calcd for $C_{20}H_{17}FNOS^+$ 338.1009; Found 338.1035.

***S*-(2-phenyl-2-(pyridin-2-yl)ethyl) 4-chlorobenzothioate (3fa)**



Following the General Procedure with the corresponding *S*-(pyridin-2-yl) 4-chlorobenzothioate (0.2 mmol) and styrene (0.6 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 50/1) as an eluent, to yield the white solid **3fa** (60.7 mg, 86%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (ddd, *J* = 4.8, 1.6, 0.8 Hz, 1H), 7.88–7.80 (m, 2H), 7.55 (td, *J* = 7.7, 1.8 Hz, 1H), 7.39–7.33 (m, 4H), 7.33–7.26 (m, 2H), 7.24–7.19 (m, 1H), 7.17–7.10 (m, 2H), 4.40 (dd, *J* = 8.8, 6.7 Hz, 1H), 3.98 (dd, *J* = 13.3, 8.9 Hz, 1H), 3.81 (dd, *J* = 13.3, 6.7 Hz, 1H).

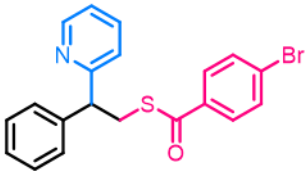
^{13}C NMR (101 MHz, $CDCl_3$) δ 190.91, 161.3, 149.3, 142.3, 139.7, 136.5, 135.4, 128.8, 128.7, 128.6, 128.1, 127.1, 123.8, 121.9, 52.9, 33.8.

IR (KBr disc, cm^{-1}): 3061, 3006, 2930, 2361, 2337, 1736, 1663, 1587, 1488, 1431, 1396, 1204, 1171, 1090, 915, 835, 749, 698, 641, 580, 532, 475.

m.p.: 67.4-68.5 ℃.

QTOF-MS: *m/z* $[M + H]^+$ Calcd for $C_{20}H_{17}ClNOS^+$ 354.0714; Found 354.0702.

***S*-(2-phenyl-2-(pyridin-2-yl)ethyl) 4-bromobenzothioate (3ga)**



Following the General Procedure with the corresponding *S*-(pyridin-2-yl) 4-bromobenzothioate (0.2 mmol) and styrene (0.6 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 50/1) as an eluent, to yield the white solid **3ga** (52.4 mg, 66%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (ddd, *J* = 4.8, 1.6, 0.8 Hz, 1H), 7.79–7.73 (m, 2H), 7.57–7.49 (m, 3H), 7.37 (dd, *J* = 5.1, 3.5 Hz, 2H), 7.33–7.26 (m, 2H), 7.24–7.18 (m, 1H), 7.12 (ddd, *J* = 7.9, 5.9, 4.4 Hz, 2H), 4.39 (dd, *J* = 8.9, 6.7 Hz, 1H), 3.98 (dd, *J* = 13.3, 8.9 Hz, 1H), 3.82 (dd, *J* = 13.3, 6.7 Hz, 1H).

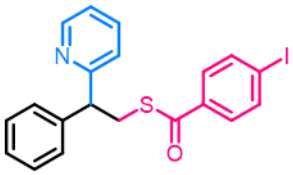
^{13}C NMR (101 MHz, $CDCl_3$) δ 191.1, 161.3, 149.3, 142.4, 136.5, 135.9, 131.8, 128.7, 128.3, 128.1, 127.1, 123.8, 121.9, 52.9, 33.8.

IR (KBr disc, cm^{-1}): 3060, 3026, 2922, 2850, 2361, 1653, 1581, 1568, 1452, 1432, 1415, 1395, 1275, 1203, 1168, 1067, 1010, 993, 912, 829, 747, 718, 697, 638, 589, 439, 416.

m.p.: 72.9-74.4 ℃.

QTOF-MS: *m/z* $[M + H]^+$ Calcd for $C_{20}H_{17}BrNOS^+$ 398.0209; Found 398.0223.

***S*-(2-phenyl-2-(pyridin-2-yl)ethyl) 4-iodobenzothioate (3ha)**



Following the General Procedure with the corresponding *S*-(pyridin-2-yl) 4-iodobenzothioate (0.2 mmol) and styrene (0.6 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 50/1) as an eluent, to yield the white solid **3ha** (45.4 mg, 51%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (ddd, *J* = 4.8, 1.6, 1.0 Hz, 1H), 7.79–7.74 (m, 2H), 7.64–7.60 (m, 2H), 7.57 (td, *J* = 7.7, 1.8 Hz, 1H), 7.36 (dd, *J* = 8.2, 1.2 Hz, 2H), 7.33–7.27 (m, 2H), 7.25–7.19 (m, 1H), 7.17–7.11 (m, 2H), 4.39 (dd, *J* = 8.9, 6.7 Hz, 1H), 3.97 (dd, *J* = 13.3, 8.9 Hz, 1H), 3.81 (dd, *J* = 13.3, 6.7 Hz, 1H).

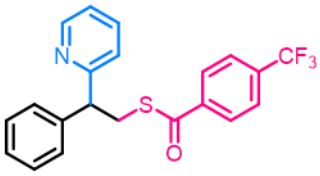
^{13}C NMR (101 MHz, $CDCl_3$) δ 191.4, 161.3, 149.24 142.3, 137.8, 136.5, 136.4, 128.7, 128.6, 128.1, 127.1, 123.8, 121.9, 101.0, 52.9, 33.8.

IR (KBr disc, cm^{-1}): 3393, 3184, 3054, 2920, 2850, 2360, 1956, 1729, 1652, 1580, 1491, 1470, 1453, 1427, 1388, 1274, 1203, 1174, 1147, 1121, 1076, 1054, 1033, 1002, 908, 819, 799, 746, 695, 637.

m.p.: 111.2-111.8 ℃.

QTOF-MS: *m/z* $[M + H]^+$ Calcd for $C_{20}H_{17}INOS^+$ 446.0070; Found 446.0067.

_S_-(2-phenyl-2-(pyridin-2-yl)ethyl) 4-(trifluoromethyl)benzothioate (3ia)



Following the General Procedure with the corresponding *S*-(pyridin-2-yl) 4-(trifluoromethyl)benzothioate (0.2 mmol) and styrene (0.6 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 50/1) as an eluent, to yield the white solid **3ia** (41.0 mg, 53%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (dd, *J* = 5.4, 1.4 Hz, 1H), 8.01 (d, *J* = 8.2 Hz, 2H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.58 (td, *J* = 7.7, 1.7 Hz, 1H), 7.37 (d, *J* = 7.3 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.23 (t, *J* = 7.2 Hz, 1H), 7.16 (dd, *J* = 7.5, 4.2 Hz, 2H), 4.41 (dd, *J* = 8.8, 6.8 Hz, 1H), 4.01 (dd, *J* = 13.3, 8.9 Hz, 1H), 3.85 (dd, *J* = 13.3, 6.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.2, 161.2, 149.3, 142.2, 139.9, 136.5, 134.6 (q, $^{2}J_{C\text{-}F}$ = 32.6 Hz), 128.7, 128.1, 127.6, 127.1, 125.6 (q, $^{3}J_{C\text{-}F}$ = 3.7 Hz), 123.8, 123.5 (q, $^{1}J_{C\text{-}F}$ = 272.7 Hz), 121.9, 77.4, 77.0, 76.7, 52.8, 33.9.

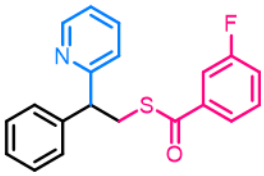
^{19}F NMR (377 MHz, $CDCl_3$) δ -63.11.

IR (KBr disc, cm^{-1}): 3672, 2971, 2927, 2361, 2337, 1656, 1540, 1514, 1473, 1433, 1402, 1322, 1228, 1174, 1131, 1066, 1017, 921, 850, 775, 748, 698, 653, 619, 473, 422.

m.p.: 55.2-56.4 ℃.

QTOF-MS: *m/z* $[M + H]^+$ Calcd for $C_{15}H_9F_3NO^+$ 388.0977; Found 388.0956.

_S_-(2-phenyl-2-(pyridin-2-yl)ethyl) 3-fluorobenzothioate (3ja)



Following the General Procedure with the corresponding *S*-(pyridin-2-yl) 3-fluorobenzothioate (0.2 mmol) and styrene (0.6 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 50/1) as an eluent, to yield the white solid **3ja** (47.9 mg, 71%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 4.2 Hz, 1H), 7.69 (d, *J* = 7.8 Hz, 1H), 7.62–7.57 (m, 1H), 7.54 (td, *J* = 7.7, 1.8 Hz, 1H), 7.35 (dd, *J* = 11.2, 5.0 Hz, 3H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.21 (ddd, *J* = 10.7, 7.5, 2.4 Hz, 2H), 7.17–7.09 (m, 2H), 4.40 (dd, *J* = 8.8, 6.8 Hz, 1H), 3.99 (dd, *J* = 13.3, 8.9 Hz, 1H), 3.83 (dd, *J* = 13.3, 6.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 189.8 (d, $^{4}J_{C\text{-}F}$ = 2.6 Hz), 161.6 (d, $^{1}J_{C\text{-}F}$ = 248.3 Hz), 160.3, 148.2, 141.3, 138.1 (d, $^{3}J_{C\text{-}F}$ = 6.6 Hz), 135.4, 129.1 (d, $^{3}J_{C\text{-}F}$ = 7.8 Hz), 127.6, 127.0, 126.0, 122.7, 122.0

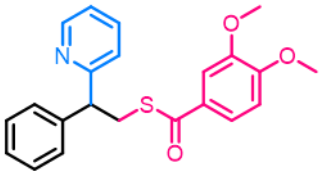
(d, $^4J_{C\text{-}F}$ = 3.1 Hz), 120.8, 119.1 (d, $^2J_{C\text{-}F}$ = 21.3 Hz), 113.0 (d, $^2J_{C\text{-}F}$ = 23.1 Hz), 51.8, 32.8. ^{19}F NMR (377 MHz, $CDCl_3$) δ -111.69.

IR (KBr disc, cm^{-1}): 3853, 3742, 3061, 2929, 2359, 1658, 1580, 1466, 1430, 1302, 1204, 1174, 1086, 995, 909, 760, 687, 645.

m.p.: 73.4-74.4 ℃.

QTOF-MS: *m/z* $[M + H]^+$ Calcd for $C_{20}H_{17}FNOS^+$ 338.1009; Found 338.1022.

_S_-(2-phenyl-2-(pyridin-2-yl)ethyl) 3,4-dimethoxybenzothioate (3ka)



Following the General Procedure with the corresponding *S*-(pyridin-2-yl) 3,4-dimethoxybenzothioate (0.2 mmol) and styrene (0.6 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 50/1) as an eluent, to yield the transparent oil **3ka** (48.5 mg, 64%).

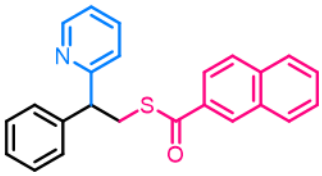
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (dd, *J* = 4.7, 0.6 Hz, 1H), 7.59 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.58–7.52 (m, 1H), 7.44 (d, *J* = 2.0 Hz, 1H), 7.40–7.35 (m, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.24–7.19 (m, 1H), 7.16 (d, *J* = 7.8 Hz, 1H), 7.15–7.10 (m, 1H), 6.82 (d, *J* = 8.5 Hz, 1H), 4.41 (dd, *J* = 8.8, 6.7 Hz, 1H), 3.96 (dd, *J* = 13.3, 8.9 Hz, 1H), 3.90 (s, 3H), 3.90 (s, 3H), 3.80 (dd, *J* = 13.3, 6.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.8, 161.5, 153.4, 149.3, 148.9, 142.6, 136.5, 130.1, 128.6, 128.1, 127.0, 123.8, 121.8, 121.7, 110.2, 109.5, 56.1, 56.0, 53.1, 33.8.

IR (KBr disc, cm^{-1}): 3004, 2959, 2934, 2867, 2837, 2610, 1652, 1584, 1512, 1453, 1433, 1413, 1340, 1262, 1195, 1160, 1139, 1021, 990, 965, 911, 873, 847, 811, 761, 730, 699, 658, 646, 624, 602, 533, 443, 414.

QTOF-MS: *m/z* $[M + H]^+$ Calcd for $C_{22}H_{22}NO_3S^+$ 380.1315; Found 380.1316.

_S_-(2-phenyl-2-(pyridin-2-yl)ethyl) naphthalene-2-carbothioate (3la)



Following the General Procedure with the corresponding *S*-(pyridin-2-yl) naphthalene-2-carbothioate (0.2 mmol) and styrene (0.6 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 50/1) as an eluent, to yield the white solid **3la** (39.1 mg, 53%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (dd, *J* = 4.9, 0.8 Hz, 1H), 8.47 (s, 1H), 7.95 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.83 (d, *J* = 8.6 Hz, 2H), 7.60–7.48 (m, 3H), 7.43–7.37 (m, 2H),

7.32 (t, *J* = 7.5 Hz, 2H), 7.23 (ddd, *J* = 8.7, 4.5, 1.3 Hz, 1H), 7.18 (d, *J* = 7.8 Hz, 1H), 7.16–7.12 (m, 1H), 4.46 (dd, *J* = 8.8, 6.8 Hz, 1H), 4.03 (dd, *J* = 13.3, 8.9 Hz, 1H), 3.88 (dd, *J* = 13.3, 6.7 Hz, 1H).

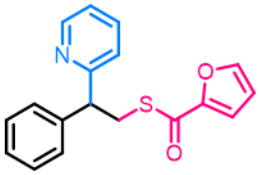
^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 161.5, 149.3, 142.5, 136.5, 135.7, 134.4, 132.4, 129.6, 128.7, 128.7, 128.4, 128.4, 128.1, 127.8, 127.1, 126.9, 123.8, 123.2, 121.8, 53.0, 33.9.

IR (KBr disc, cm^{-1}): 3083, 3059, 2990, 2920, 2850, 1642, 1602, 1569, 1492, 1467, 1433, 1416, 1350, 1276, 1254, 1222, 1173, 1148, 1120, 964, 908, 869, 832, 750, 690, 642, 458, 432, 419, 403.

m.p.: 126.0-127.1 ℃.

QTOF-MS: *m/z* $[M + H]^+$ Calcd for $C_{24}H_{20}NOS^+$ 370.1260; Found 370.1238.

***S*-(2-phenyl-2-(pyridin-2-yl)ethyl) furan-2-carbothioate (3ma)**



Following the General Procedure with the corresponding *S*-(pyridin-2-yl) furan-2-carbothioate (0.2 mmol) and styrene (0.6 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 50/1) as an eluent, to yield the transparent oil **3ma** (37.1 mg, 60%).

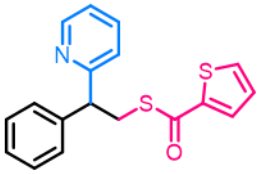
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (dd, *J* = 4.8, 0.7 Hz, 1H), 7.56 (td, *J* = 7.7, 1.8 Hz, 1H), 7.53–7.50 (m, 1H), 7.36 (d, *J* = 7.3 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.18–7.10 (m, 3H), 6.48 (dd, *J* = 3.6, 1.7 Hz, 1H), 4.39 (dd, *J* = 8.9, 6.7 Hz, 1H), 3.94 (dd, *J* = 13.3, 9.0 Hz, 1H), 3.80 (dd, *J* = 13.3, 6.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 180.7, 161.3, 150.9, 149.2, 146.1, 142.4, 136.5, 128.7, 128.1, 127.1, 123.8, 121.8, 115.5, 112.2, 53.0, 32.8.

IR (KBr disc, cm^{-1}): 3674, 2983, 2923, 2361, 1717, 1647, 1586, 1562, 1465, 1431, 1382, 1249, 1150, 1074, 1013, 953, 847, 751, 696, 594, 532, 420.

QTOF-MS: *m/z* $[M + Na]^+$ Calcd for $C_{18}H_{15}NNaO_2S^+$ 332.0716; Found 332.0713.

***S*-(2-phenyl-2-(pyridin-2-yl)ethyl) thiophene-2-carbothioate (3na)**



Following the General Procedure with the corresponding *S*-(pyridin-2-yl) thiophene-2-carbothioate (0.2 mmol) and styrene (0.6 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 50/1) as an eluent, to yield the white solid **3na** (41.0 mg, 64%).

^{1}H NMR (400 MHz, $CDCl_3$) 8.62 (d, *J* = 4.1 Hz, 1H), 7.71 (dd, *J* = 3.8, 1.0 Hz, 1H), 7.58–7.53 (m, 2H), 7.36 (d, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.18–7.10 (m, 2H),

7.04 (dd, *J* = 4.8, 3.9 Hz, 1H), 4.42 (dd, *J* = 8.9, 6.6 Hz, 1H), 3.96 (dd, *J* = 13.3, 9.0 Hz, 1H), 3.81 (dd, *J* = 13.3, 6.6 Hz, 1H).

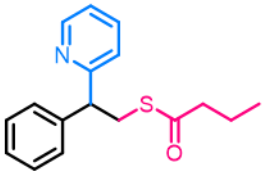
^{13}C NMR (101 MHz, $CDCl_3$) δ 184.2, 161.3, 149.2, 142.4, 142.2, 136.5, 132.6, 131.1, 128.7, 128.1, 127.8, 127.1, 123.9, 121.8, 53.0, 33.8.

IR (KBr disc, cm^{-1}): 3612, 2984, 2904, 2361, 2337, 1650, 1541, 1513, 1410, 1229, 1204, 1072, 1051, 895, 816, 696, 421.

m.p.: 77.8-78.4 ℃.

QTOF-MS: *m/z* $[M + Na]^+$ Calcd for $C_{18}H_{15}NNaOS_2^+$ 348.0487; Found 348.0508.

_S_-(2-phenyl-2-(pyridin-2-yl)ethyl) butanethioate (3oa)



Following the General Procedure with the corresponding *S*-(pyridin-2-yl) butanethioate (0.2 mmol) and styrene (0.6 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 50/1) as an eluent, to yield the transparent oil **3oa** (49.6 mg, 87%).

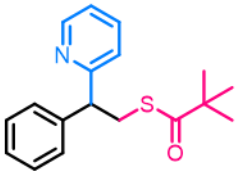
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (ddd, *J* = 4.8, 1.6, 0.8 Hz, 1H), 7.55 (td, *J* = 7.7, 1.8 Hz, 1H), 7.35–7.24 (m, 4H), 7.23–7.17 (m, 1H), 7.12 (ddd, *J* = 5.9, 4.9, 2.4 Hz, 2H), 4.28 (dd, *J* = 8.7, 7.0 Hz, 1H), 3.76 (dd, *J* = 13.3, 8.8 Hz, 1H), 3.63 (dd, *J* = 13.3, 6.9 Hz, 1H), 2.51–2.42 (m, 2H), 1.71–1.57 (m, 2H), 0.89 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.5, 161.5, 149.2, 142.3, 136.5, 128.6, 128.1, 127.0, 123.6, 121.8, 53.0, 45.9, 33.5, 19.2, 13.5.

IR (KBr disc, cm^{-1}): 3006, 2964, 2933, 2874, 1683, 1589, 1569, 1493, 1472, 1453, 1433, 1381, 1292, 1274, 1222, 1145, 1114, 1051, 994, 886, 797, 752, 698, 617, 597, 538, 414.

QTOF-MS: *m/z* $[M + H]^+$ Calcd for $C_{17}H_{20}NOS^+$ 286.1260; Found 286.1255.

_S_-(2-phenyl-2-(pyridin-2-yl)ethyl) 2,2-dimethylpropanethioate (3pa)



Following the General Procedure with the corresponding *S*-(pyridin-2-yl) 2,2-dimethylpropanethioate (0.2 mmol) and styrene (0.6 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 50/1) as an eluent, to yield the transparent oil **3pa** (32.3 mg, 54%).

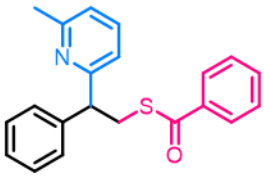
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (ddd, *J* = 4.8, 1.7, 0.9 Hz, 1H), 7.60–7.52 (m, 1H), 7.30 (ddd, *J* = 15.5, 8.5, 4.2 Hz, 4H), 7.21 (d, *J* = 7.1 Hz, 1H), 7.14 (dd, *J* = 7.6, 2.5 Hz, 2H), 4.26 (s, 1H), 3.74 (dd, *J* = 13.4, 8.7 Hz, 1H), 3.57 (dd, *J* = 13.4, 6.9 Hz, 1H), 1.17 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 206.9, 161.7, 149.2, 142.4, 136.4, 128.5, 128.1, 126.9, 123.6, 121.7, 53.0, 46.4, 33.3, 27.4.

IR (KBr disc, cm^{-1}): 3004, 2959, 2934, 2867, 1642, 1602, 1569, 1492, 1467, 1433, 965, 911, 873, 847, 811, 761, 730, 699, 658, 646, 624, 602, 533, 443, 414.

QTOF-MS: *m/z* $[M + H]^+$ Calcd for $C_{18}H_{22}NOS^+$ 300.1417; Found 300.1398.

***S*-(2-(6-methylpyridin-2-yl)-2-phenylethyl) benzothioate (3qa)**



Following the General Procedure with the corresponding *S*-(6-methylpyridin-2-yl) benzothioate (0.2 mmol) and styrene (0.6 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 50/1) as an eluent, to yield the white solid **3qa** (56.6 mg, 85%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.1 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.45 (d, *J* = 7.7 Hz, 1H), 7.43–7.36 (m, 4H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 6.96 (dd, *J* = 16.0, 7.7 Hz, 2H), 4.36 (dd, *J* = 8.5, 7.1 Hz, 1H), 3.97 (dd, *J* = 13.2, 8.7 Hz, 1H), 3.81 (dd, *J* = 13.2, 6.9 Hz, 1H), 2.57 (s, 3H).

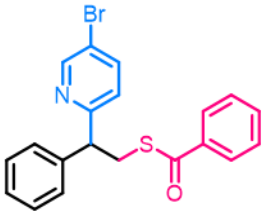
^{13}C NMR (101 MHz, $CDCl_3$) δ 192.2, 160.7, 157.9, 142.6, 137.2, 136.5, 133.2, 128.5, 128.5, 128.2, 127.2, 126.9, 121.2, 120.3, 52.9, 33.9, 24.7.

IR (KBr disc, cm^{-1}): 3360, 2979, 2902, 2360, 2335, 1657, 1588, 1513, 1432, 1399, 1205, 1049, 906, 883, 818, 748, 721, 687, 490, 452, 421.

m.p.: 84.6-85.1 ℃.

QTOF-MS: *m/z* $[M + Na]^+$ Calcd for $C_{21}H_{19}NNaOS^+$ 356.1080; Found 356.1085.

***S*-(2-(5-bromopyridin-2-yl)-2-phenylethyl) benzothioate (3ra)**



Following the General Procedure with the corresponding *S*-(5-bromopyridin-2-yl) benzothioate (0.2 mmol) and styrene (0.6 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 50/1) as an eluent, to yield the white solid **3ra** (57.3 mg, 72%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (s, 1H), 7.91 (d, *J* = 7.5 Hz, 2H), 7.67 (dt, *J* = 8.3, 2.3 Hz, 1H), 7.57–7.48 (m, 1H), 7.40 (t, *J* = 6.8 Hz, 2H), 7.37–7.26 (m, 4H), 7.26–7.18 (m, 1H), 7.05 (dd, *J* =

8.3, 1.6 Hz, 1H), 4.37 (dd, *J* = 11.1, 4.2 Hz, 1H), 3.92 (ddd, *J* = 13.1, 9.1, 2.2 Hz, 1H), 3.78 (ddd, *J* = 13.4, 6.4, 2.2 Hz, 1H).

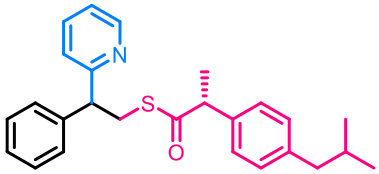
^{13}C NMR (101 MHz, $CDCl_3$) δ 191.9, 160.1, 150.3, 142.0, 139.1, 137.0, 133.4, 128.8, 128.6, 128.0, 127.3, 125.1, 118.9, 52.5, 33.6.

IR (KBr disc, cm^{-1}): 3059, 3030, 2926, 2853, 2169, 1898, 1819, 1659, 1579, 1459, 1371, 1308, 1206, 1094, 1005, 913, 830, 771, 736, 691, 647.

m.p.: 110.8-111.9 ℃.

QTOF-MS: *m/z* $[M + H]^+$ Calcd for $C_{20}H_{17}BrNOS^+$ 398.0209; Found 398.0208.

_S_-(2-phenyl-2-(pyridin-2-yl)ethyl) (2_R_)-2-(4-isobutylphenyl)propanethioate (3sa)



Following the General Procedure with the corresponding *S*-(pyridin-2-yl) (*R*)-2-(4-isobutylphenyl)propanethioate (0.2 mmol) and styrene (0.6 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 50/1) as an eluent, to yield the transparent oil **3sa** (48.4 mg, 60%).

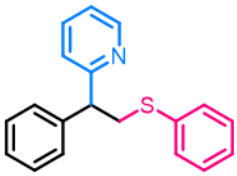
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 4.0 Hz, 1H), 7.48 (dtd, *J* = 11.7, 7.7, 1.8 Hz, 1H), 7.30–7.21 (m, 4H), 7.21–7.10 (m, 3H), 7.10–6.98 (m, 4H), 4.22 (dd, *J* = 16.1, 8.9 Hz, 1H), 3.84–3.75 (m, 1H), 3.75–3.67 (m, 1H), 3.56 (ddd, *J* = 13.4, 6.9, 2.7 Hz, 1H), 2.44 (d, *J* = 7.2 Hz, 2H), 1.83 (td, *J* = 13.5, 6.7 Hz, 1H), 1.46 (d, *J* = 7.1 Hz, 3H), 0.94–0.83 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.2, 161.5, 161.5, 149.2, 149.2, 142.4, 142.3, 140.8, 140.8, 137.1, 137.1, 136.4, 136.3, 129.4, 129.3, 128.5, 128.1, 127.6, 126.9, 123.6, 123.6, 121.7, 53.9, 53.8, 52.9, 52.8, 45.1, 33.8, 33.8, 30.2, 22.4, 18.5, 18.4.

IR (KBr disc, cm^{-1}): 2954, 2929, 2868, 2350, 1680, 1589, 1569, 1511, 1493, 1469, 1453, 1433, 1383, 1367, 1276, 1022, 996, 946, 847, 801, 750, 698, 617, 545, 466, 441, 416.

QTOF-MS: *m/z* $[M + H]^+$ Calcd for $C_{26}H_{30}NOS^+$ 404.2043; Found 404.2040.

2-(1-phenyl-2-(phenylthio)ethyl)pyridine (4aa)



Following the General Procedure D with the corresponding *S*-(2-phenyl-2-(pyridin-2-yl)ethyl) benzothioate (0.2 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 50/1) as an eluent, to yield the transparent oil **4aa** (49.5 mg, 85%).

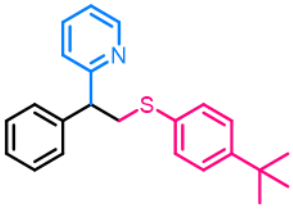
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 4.6 Hz, 1H), 7.52 (td, *J* = 7.7, 1.9 Hz, 1H), 7.31 (ddd, *J* = 11.5, 6.7, 3.5 Hz, 6H), 7.27 – 7.22 (m, 2H), 7.20 (t, *J* = 7.1 Hz, 1H), 7.15 (t, *J* = 7.3 Hz, 1H), 7.09 (t, *J* = 7.1 Hz, 2H), 4.29 (dd, *J* = 8.2, 7.1 Hz, 1H), 3.95 (dd, *J* = 12.9, 8.4 Hz, 1H), 3.57 (dd, *J* = 12.9, 6.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.7, 149.4, 142.4, 136.7, 136.4, 129.5, 128.9, 128.6, 128.1, 127.0, 126.0, 123.6, 121.8, 52.9, 38.8.

IR (KBr disc, cm^{-1}): 3058, 3026, 2926, 2350, 1587, 1570, 1493, 1472, 1433, 1331, 1291, 1273, 1197, 1088, 1072, 1052, 1026, 995, 911, 797, 739, 695, 642, 616, 595, 542, 465, 420.

QTOF-MS: *m/z* $[M + H]^+$ Calcd for $C_{19}H_{18}NS^+$ 292.1154; Found 292.1150.

2-(2-((4-(*tert*-butyl)phenyl)thio)-1-phenylethyl)pyridine (4da)



Following the General Procedure D with the corresponding *S*-(2-phenyl-2-(pyridin-2-yl)ethyl) 4-(*tert*-butyl)benzothioate (0.2 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 50/1) as an eluent, to yield the transparent oil **4da** (50.0 mg, 72%).

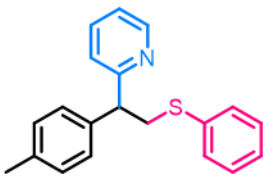
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 3.8 Hz, 1H), 7.53 (t, *J* = 7.3 Hz, 1H), 7.37–7.22 (m, 8H), 7.22–7.15 (m, 1H), 7.09 (dd, *J* = 15.3, 7.3 Hz, 2H), 4.30 (t, *J* = 7.5 Hz, 1H), 3.92 (dd, *J* = 12.7, 8.6 Hz, 1H), 3.54 (dd, *J* = 12.8, 6.7 Hz, 1H), 1.29 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.8, 149.4, 149.3, 142.5, 136.4, 132.9, 129.8, 128.6, 128.1, 126.9, 126.0, 123.6, 121.7, 53.1, 39.3, 34.5, 31.3.

IR (KBr disc, cm^{-1}): 2961, 2338, 1589, 1570, 1493, 1453, 1433, 1394, 1363, 1340, 1269, 1120, 1012, 924, 820, 743, 698, 617, 576, 491, 468, 458, 449, 431, 426, 420, 413, 402.

QTOF-MS: *m/z* $[M + H]^+$ Calcd for $C_{23}H_{26}NS^+$ 348.1780; Found 348.1781.

2-(2-(phenylthio)-1-(*p*-tolyl)ethyl)pyridine (4ab)



Following the General Procedure D with the corresponding *S*-(2-(pyridin-2-yl)-2-(*p*-tolyl)ethyl) benzothioate (0.2 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 50/1) as an eluent, to yield the transparent oil **4ab** (47.6 mg, 78%).

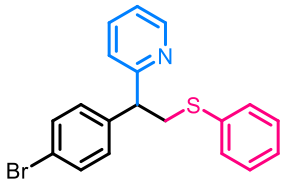
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 4.6 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 7.2 Hz, 2H), 7.28–7.19 (m, 4H), 7.18–7.12 (m, 1H), 7.10 (d, *J* = 7.4 Hz, 4H), 4.26 (t, *J* = 7.5 Hz, 1H), 3.92 (ddd, *J* = 12.7, 8.3, 1.5 Hz, 1H), 3.56 (ddd, *J* = 12.8, 7.0, 1.5 Hz, 1H), 2.29 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.9, 149.4, 139.4, 136.7, 136.6, 136.4, 129.4, 129.4, 128.9, 127.9, 125.9, 123.5, 121.7, 52.5, 38.8, 21.1.

IR (KBr disc, cm^{-1}): 3073, 3005, 2921, 2327, 1587, 1570, 1512, 1471, 1434, 1290, 1272, 1146, 1110, 1025, 995, 923, 820, 790, 738, 691, 558, 466, 443.

QTOF-MS: *m/z* $[M + H]^+$ Calcd for $C_{20}H_{20}NS^+$ 306.1311; Found 306.1308.

2-(1-(4-bromophenyl)-2-(phenylthio)ethyl)pyridine (4ag)



Following the General Procedure D with the corresponding *S*-(2-(4-bromophenyl)-2-(pyridin-2-yl)ethyl) benzothioate (0.2 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 50/1) as an eluent, to yield the transparent oil **4ag** (42.8 mg, 58%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 4.3 Hz, 1H), 7.56 (td, *J* = 7.7, 1.8 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 7.2 Hz, 2H), 7.26 (t, *J* = 7.5 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.19 – 7.15 (m, 1H), 7.12 (dd, *J* = 7.0, 5.3 Hz, 1H), 7.08 (d, *J* = 7.8 Hz, 1H), 4.22 (t, *J* = 7.6 Hz, 1H), 3.89 (dd, *J* = 13.0, 8.0 Hz, 1H), 3.53 (dd, *J* = 13.0, 7.3 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.1, 149.5, 141.3, 136.5, 136.2, 131.7, 129.9, 129.7, 128.9, 126.2, 123.5, 121.9, 120.9, 52.3, 38.8.

IR (KBr disc, cm^{-1}): 3057, 3006, 2958, 2924, 2350, 1586, 1570, 1481, 1470, 1434, 1406, 1203, 1183, 1146, 1090, 1052, 1025, 1010, 996, 822, 789, 738, 712, 690, 650, 540, 457, 435, 419, 404.

QTOF-MS: *m/z* $[M + H]^+$ Calcd for $C_{19}H_{17}BrNS^+$ 370.0260; Found 370.0252.

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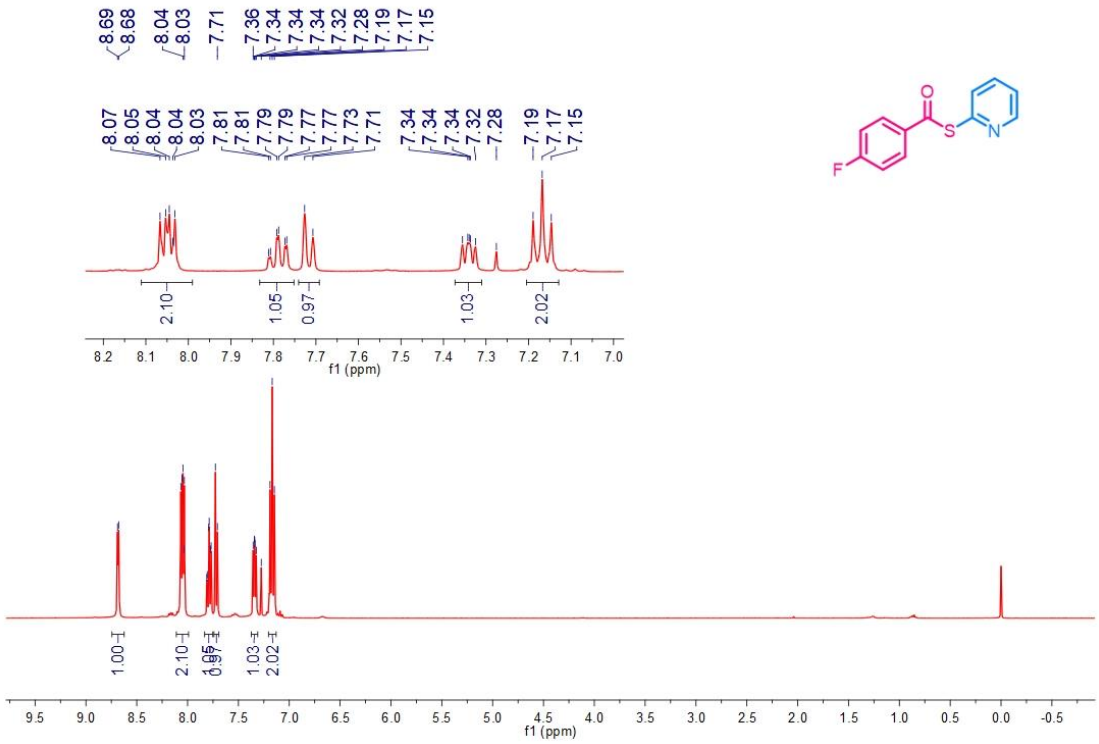
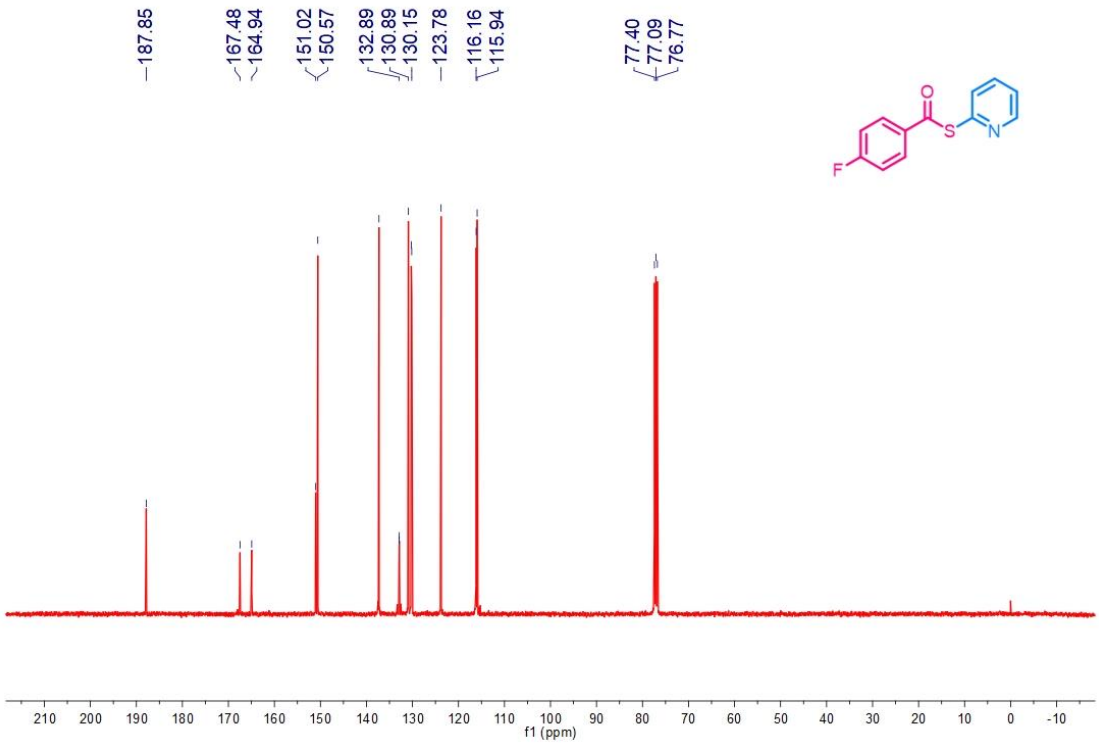
NMR Spectra

Fig. S16. The ^{1}H (400 MHz), ^{13}C (101 MHz) and ^{19}F (377 MHz) NMR spectra for *S*-(pyridin-2-yl) 4-fluorobenzothioate (**1e**) in $CDCl_3$





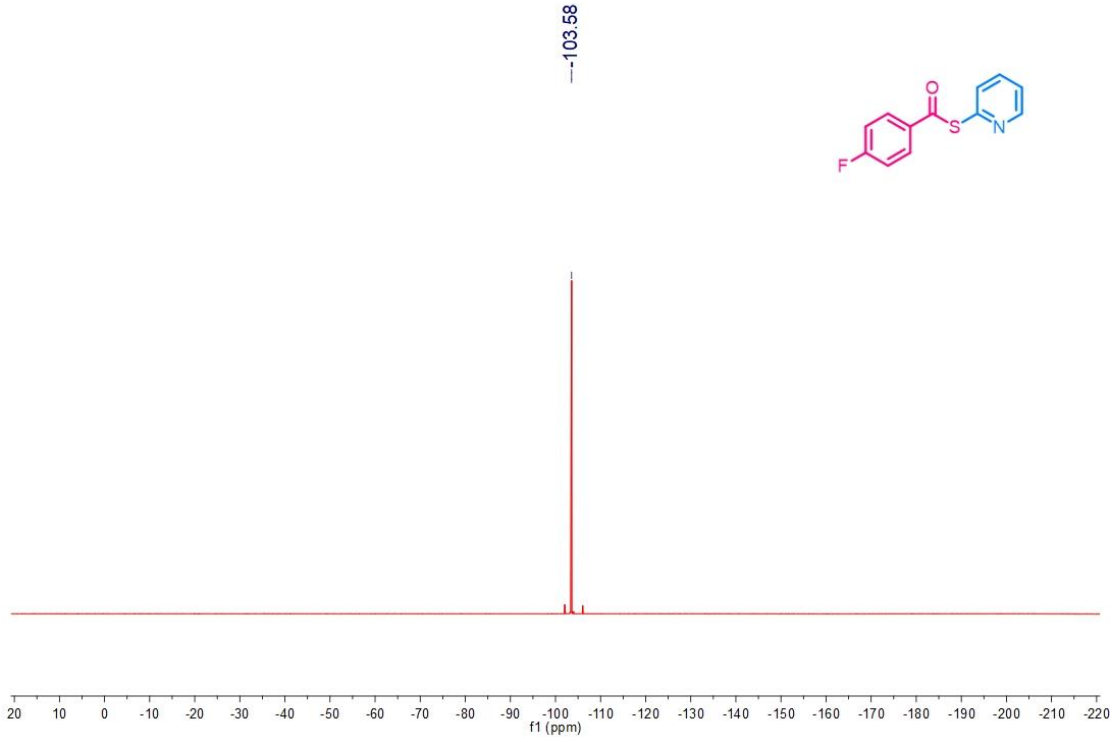
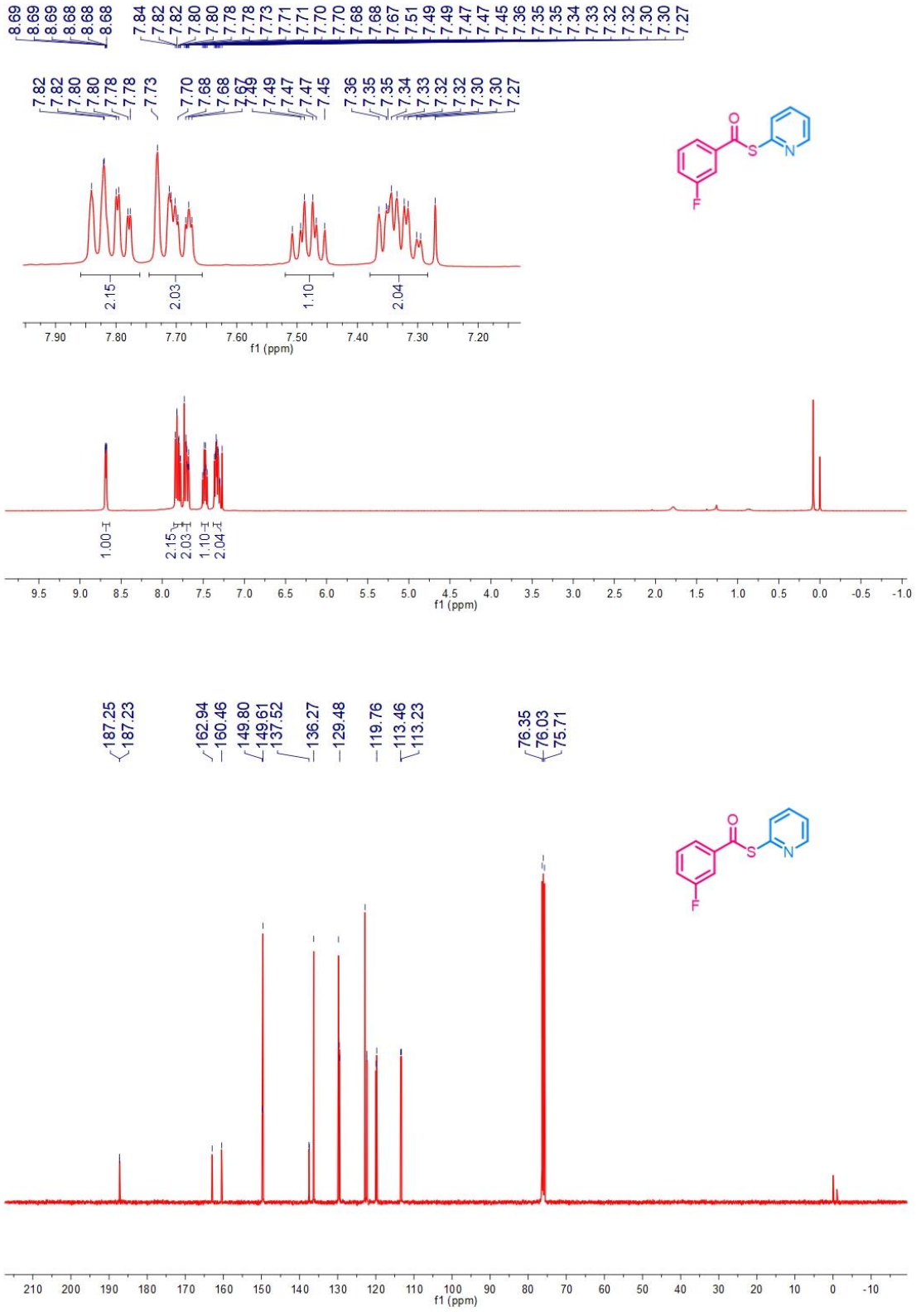
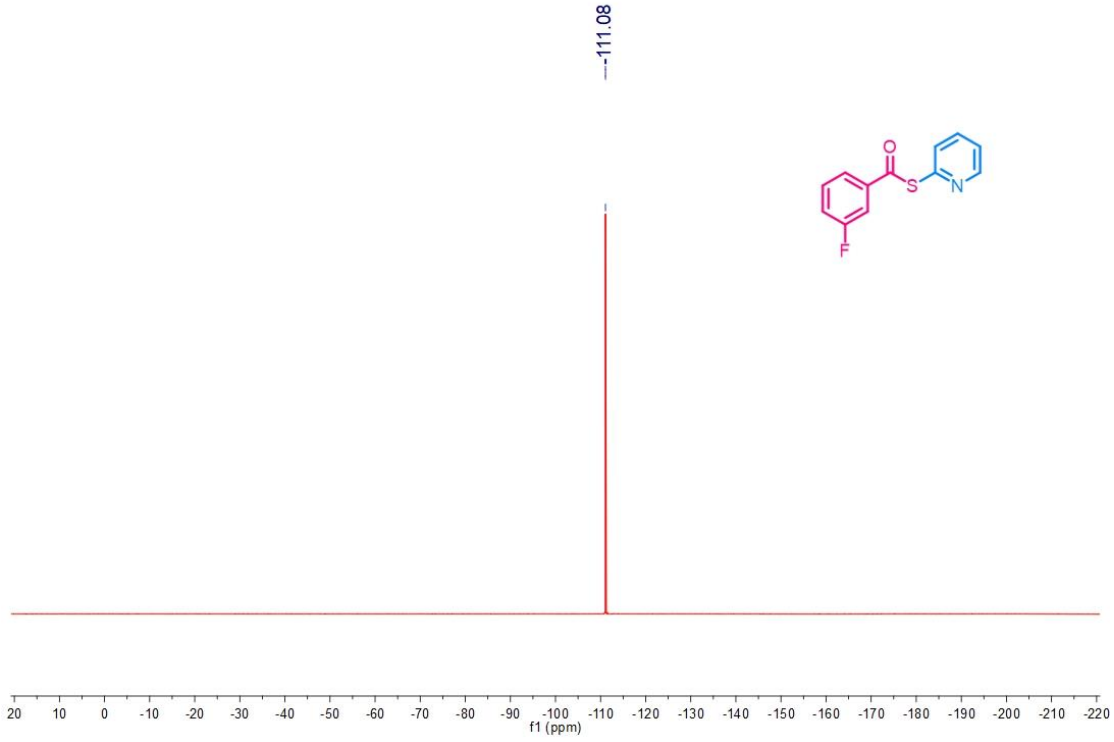

-103.58
O
S
N
F
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

Fig. S17. The ^{1}H (400 MHz), ^{13}C (101 MHz) and ^{19}F (377 MHz) NMR spectra for *S*-(pyridin-2-yl) 3-fluorobenzothioate (**1j**) in $CDCl_3$




-111.08
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20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

Fig. S18. The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for *S*-(pyridin-2-yl) 3,4-dimethoxybenzothioate (**1k**) in $CDCl_3$

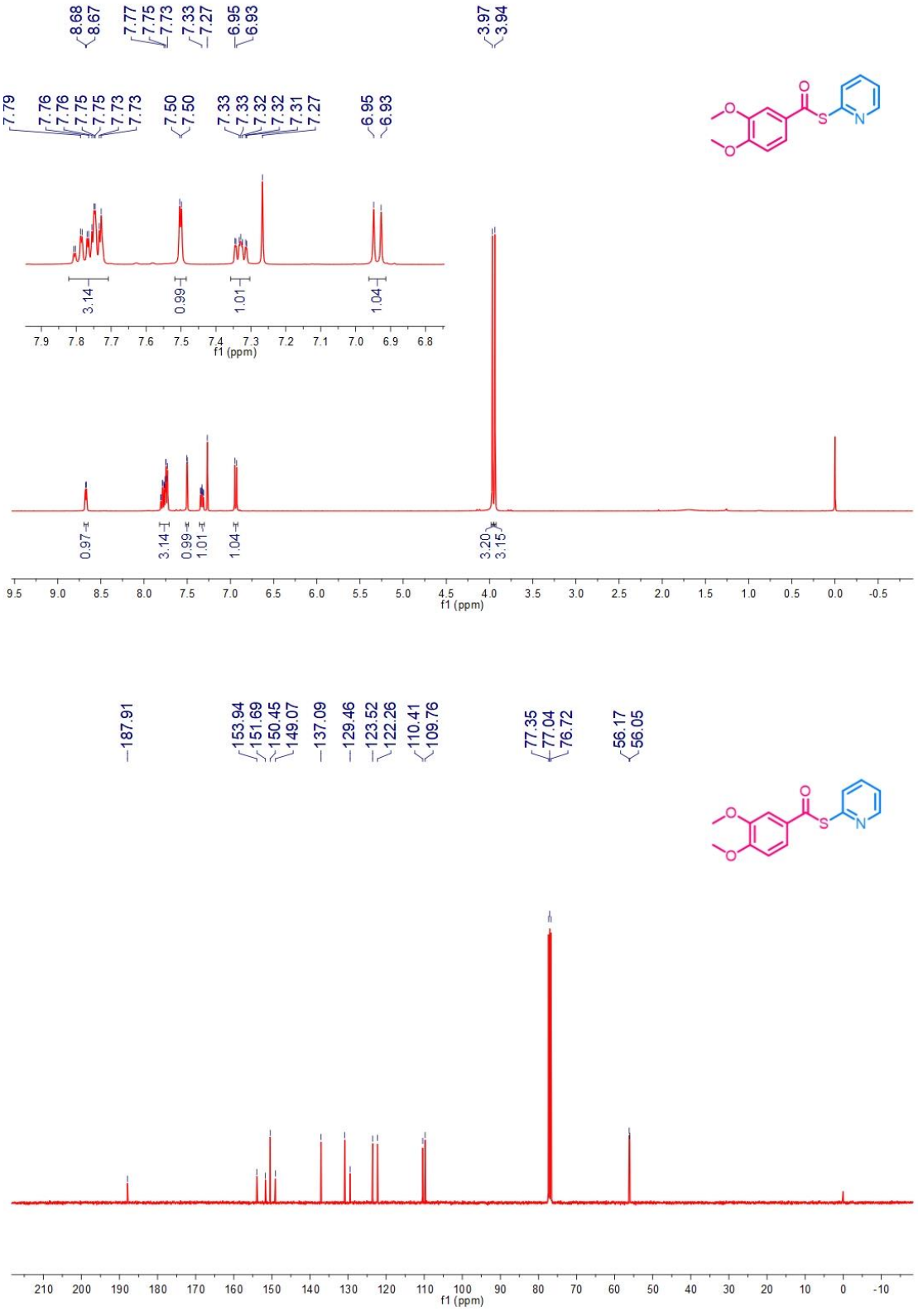
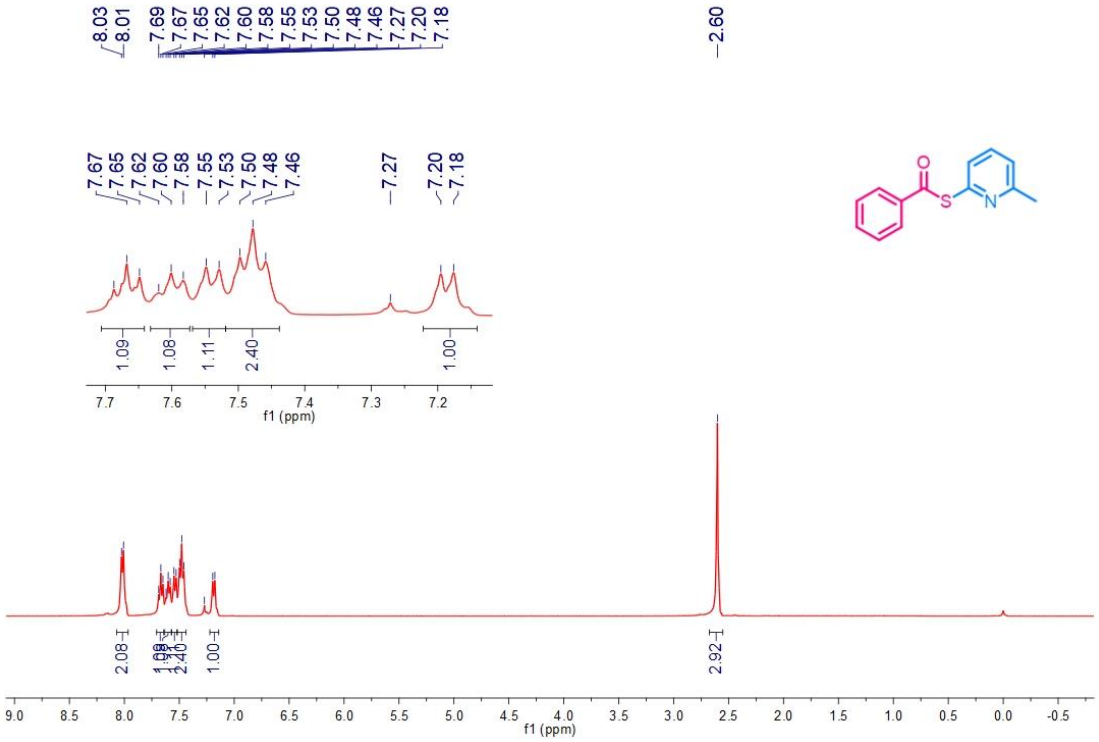


Fig. S19. The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for *S*-(6-methylpyridin-2-yl) benzothioate (**1q**) in $CDCl_3$



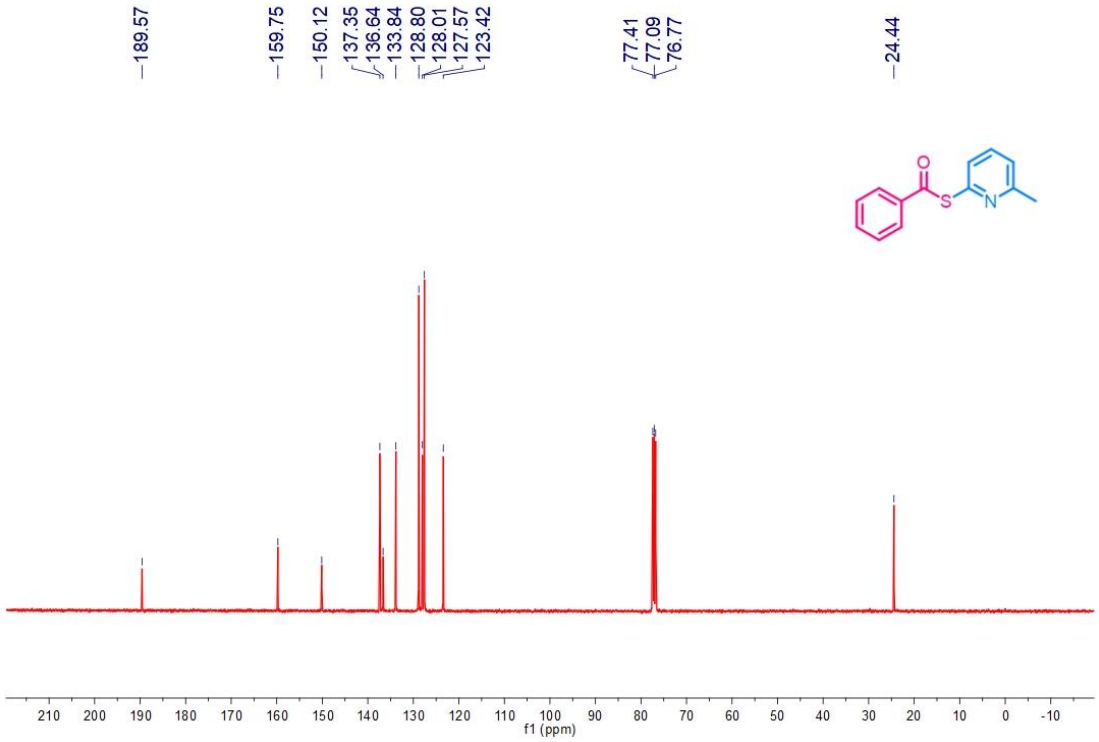


Fig. S20. The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for *S*-(5-bromopyridin-2-yl) benzothioate (**1r**) in $CDCl_3$

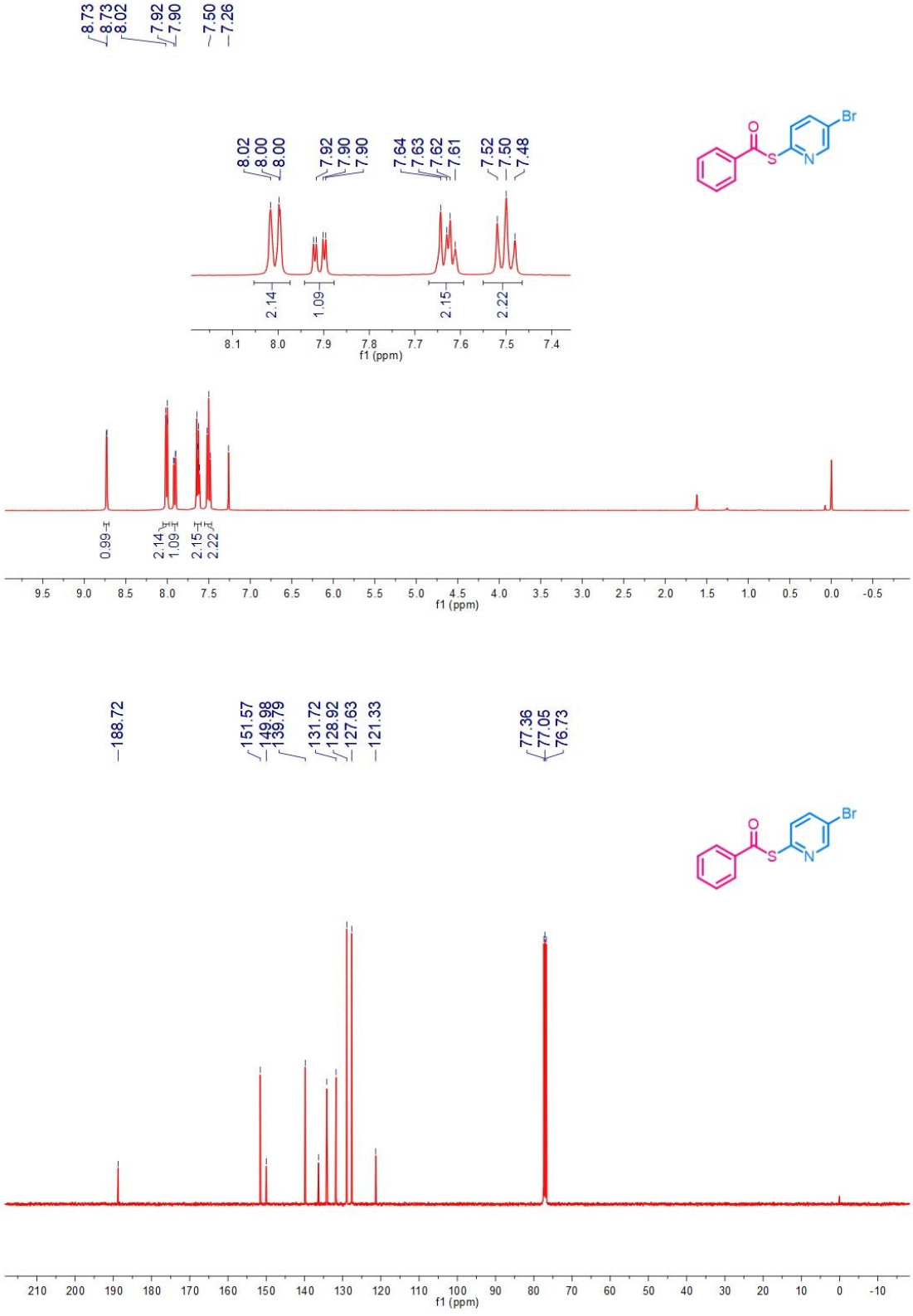
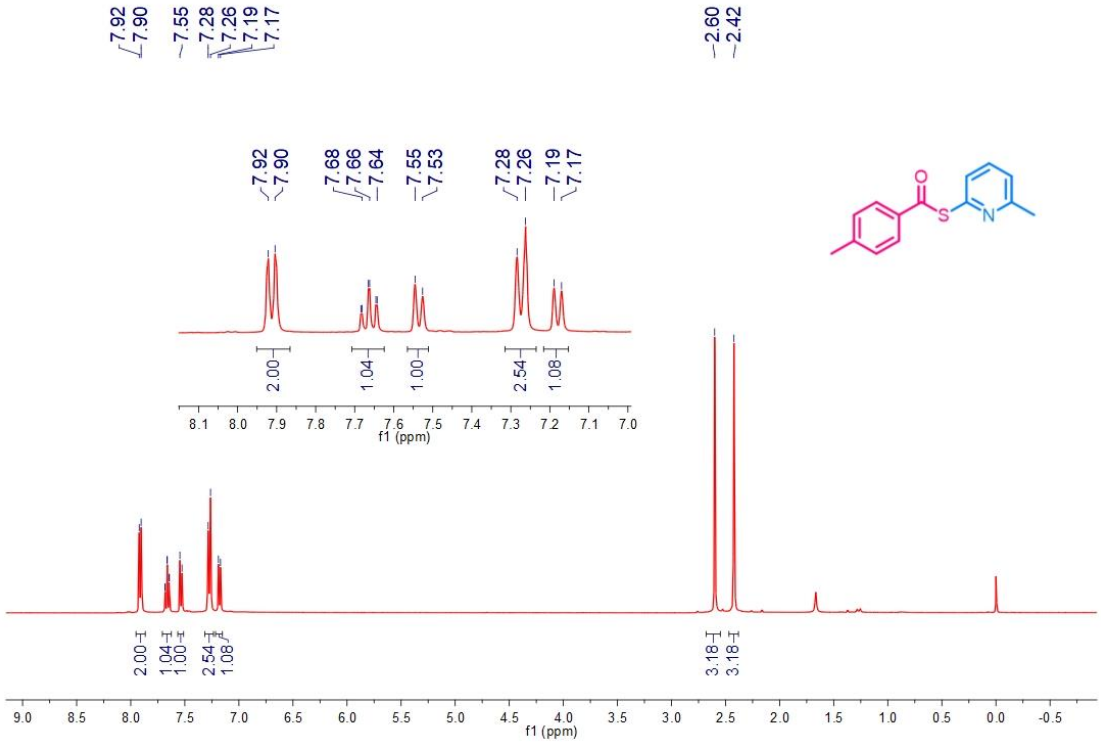


Fig. S21. The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for *S*-(6-methylpyridin-2-yl) 4-methylbenzothioate (**1t**) in $CDCl_3$



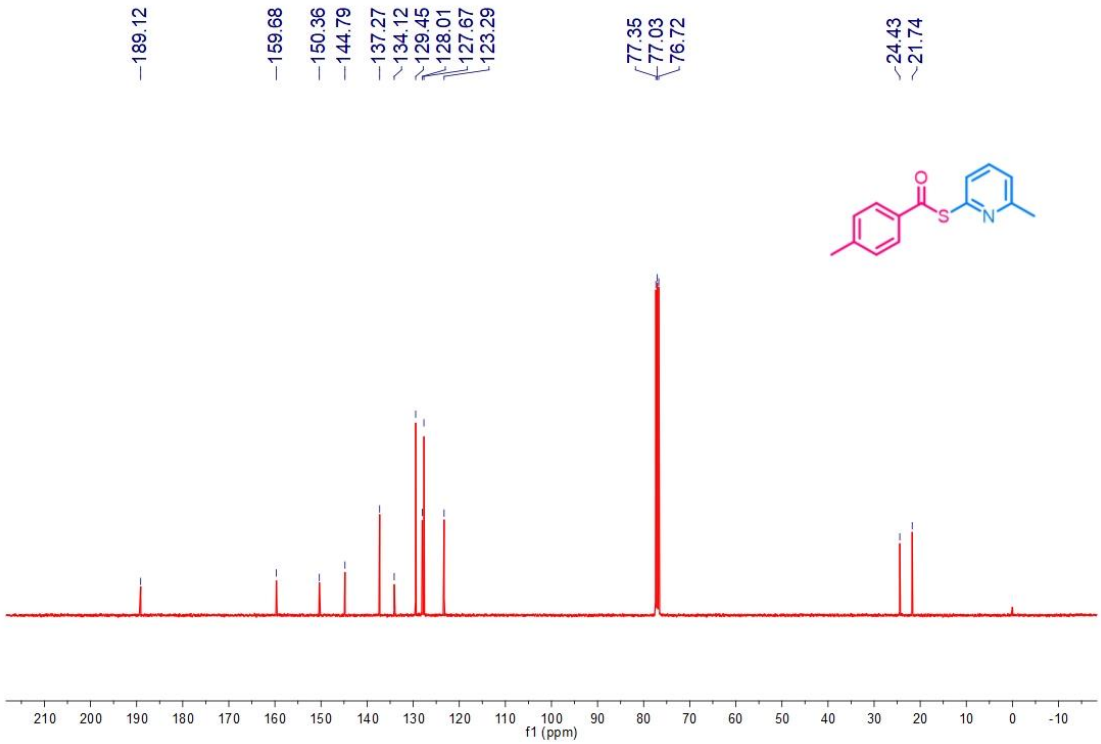


Fig. S22. The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for 4-vinylbenzyl (*R*)-2-(4-isobutylphenyl)propanoate (**2u**) in $CDCl_3$

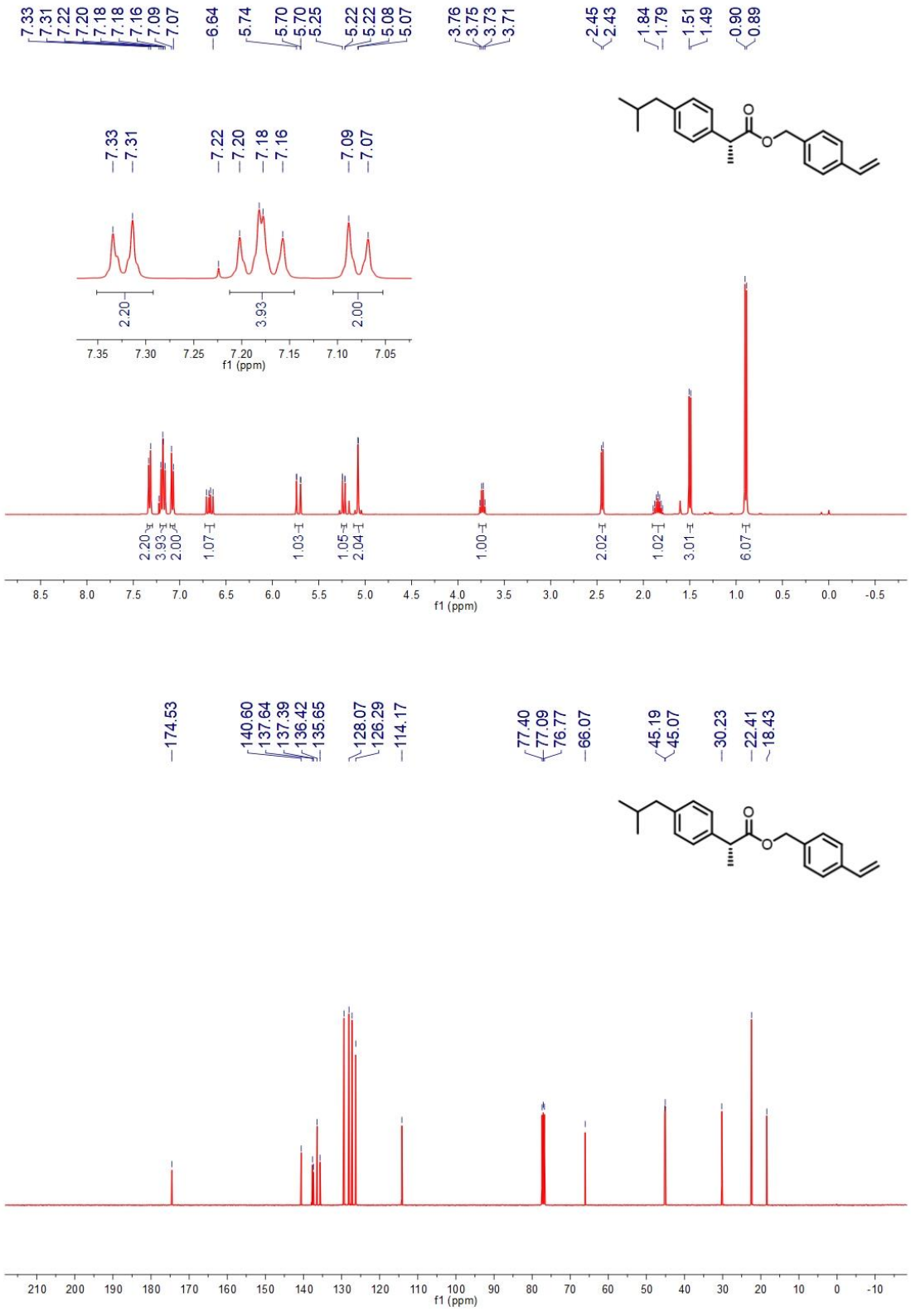


Fig. S23. The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for 4-vinylbenzyl (*S*)-2-(6-methoxynaphthalen-2-yl)propanoate (**2v**) in $CDCl_3$

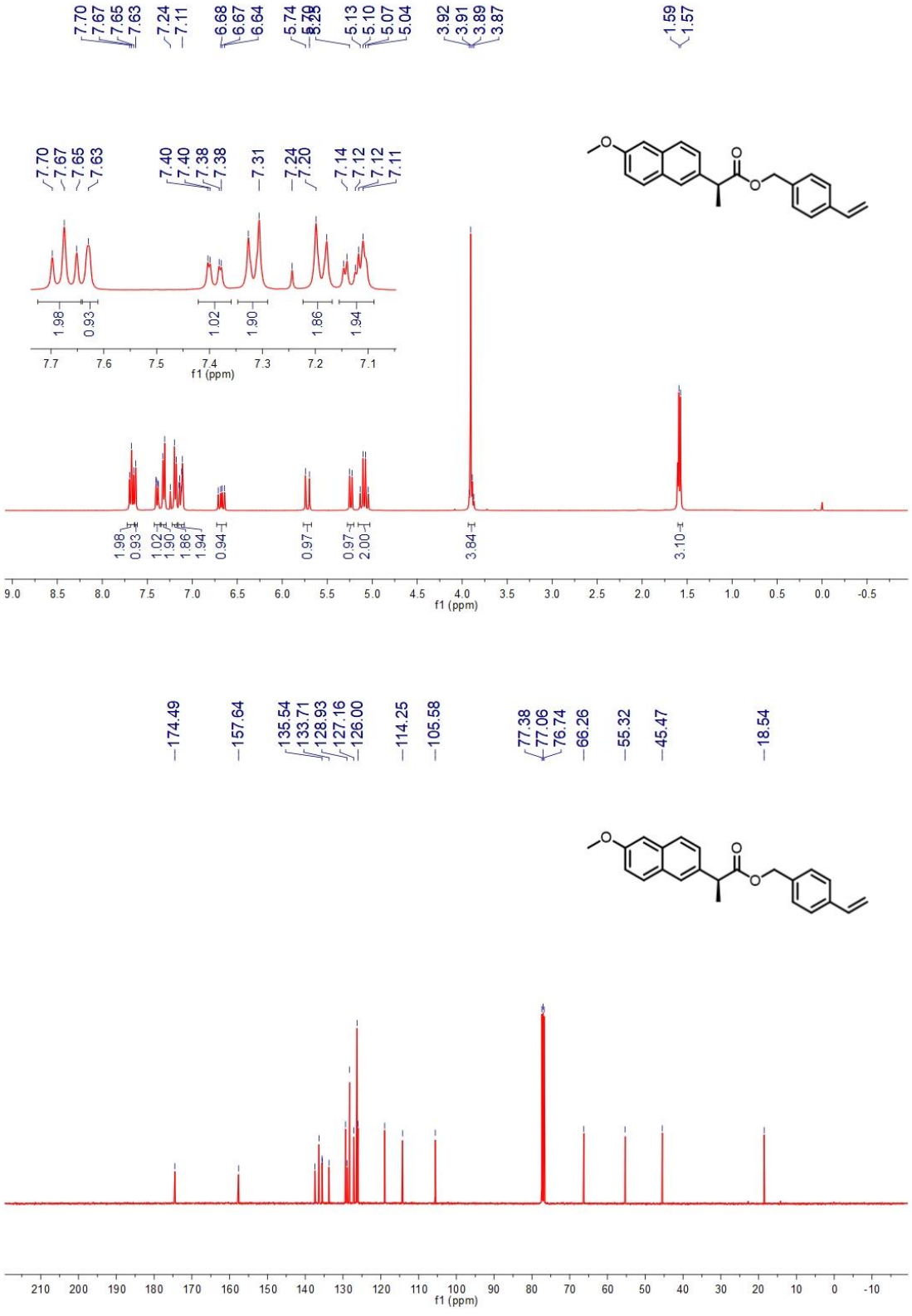


Fig. S24. The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for *S*-(2-phenyl-2-(pyridin-2-yl)ethyl) benzothioate (**3aa**) in $CDCl_3$

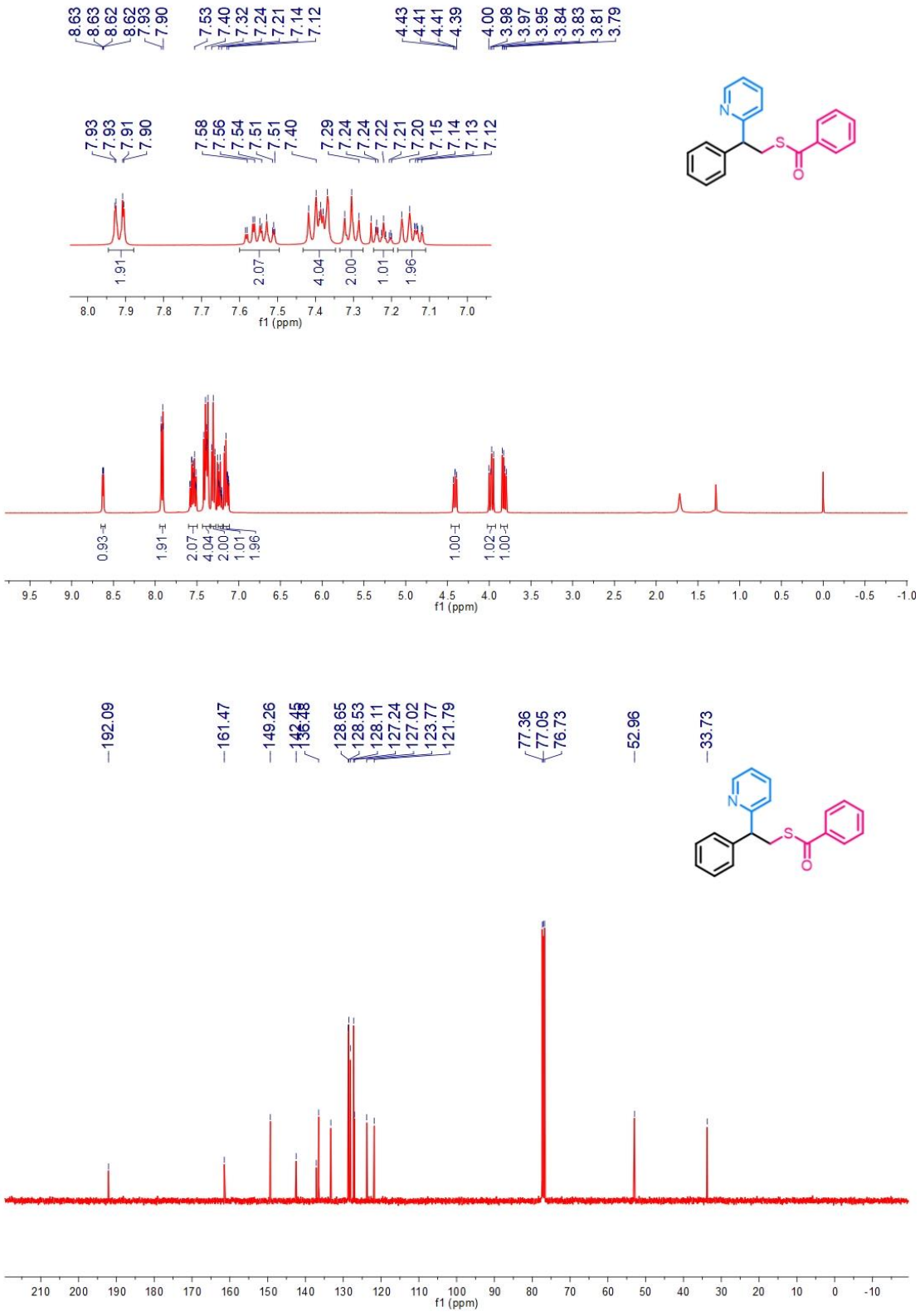


Fig. S25. The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for *S*-(2-(pyridin-2-yl)-2-(*p*-tolyl)ethyl) benzothioate (**3ab**) in $CDCl_3$

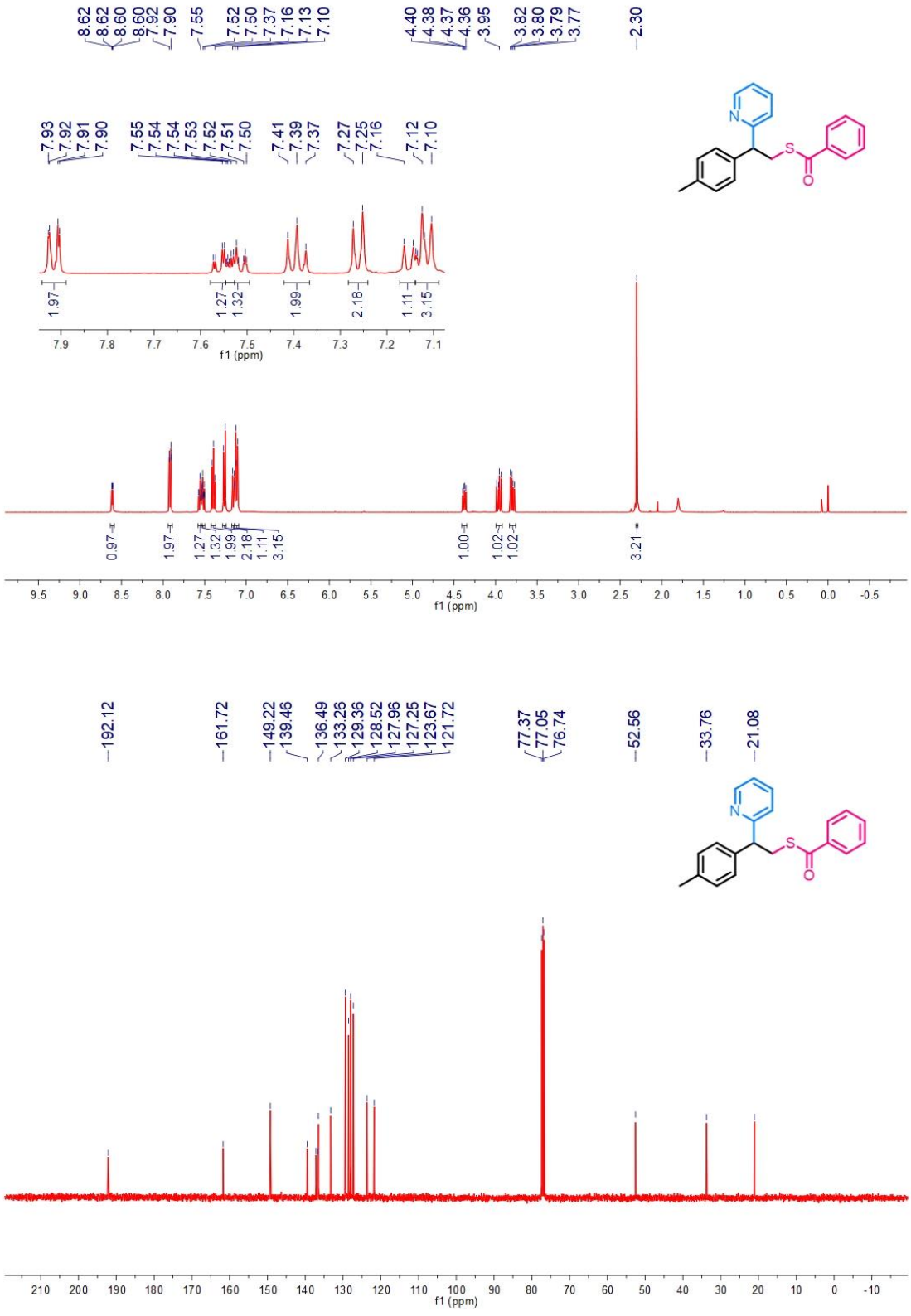
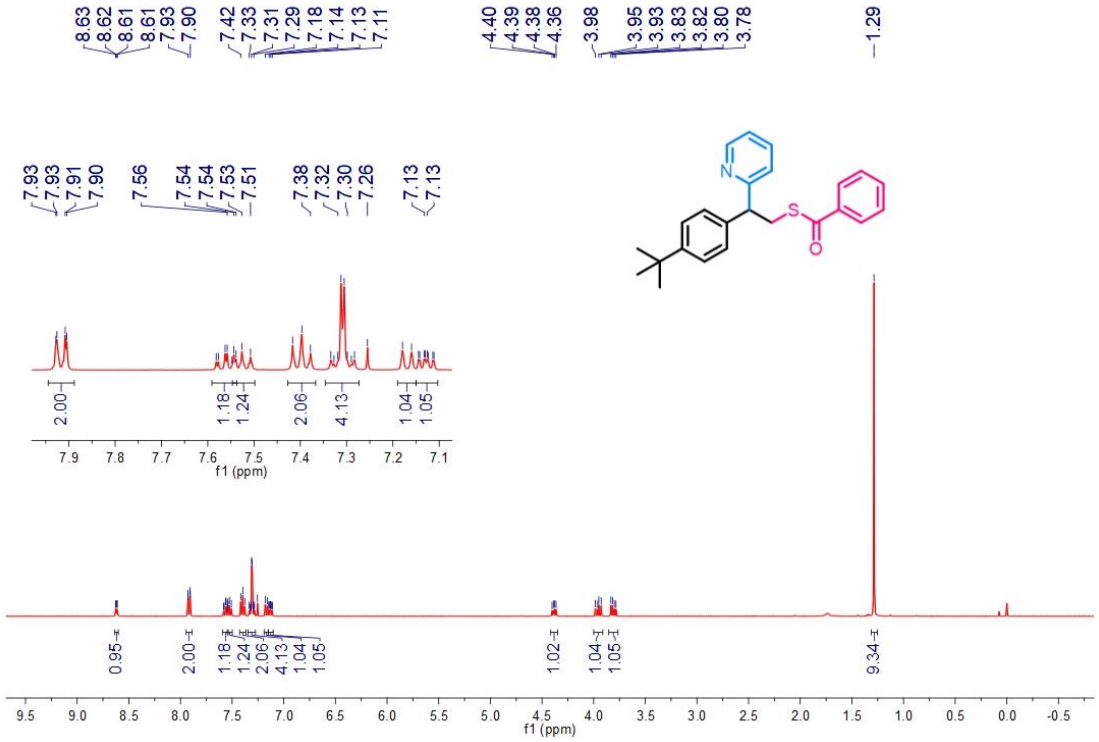


Fig. S26. The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for *S*-(2-(4-(*tert*-butyl)phenyl)-2-(pyridin-2-yl)ethyl) benzothioate (**3ac**) in $CDCl_3$



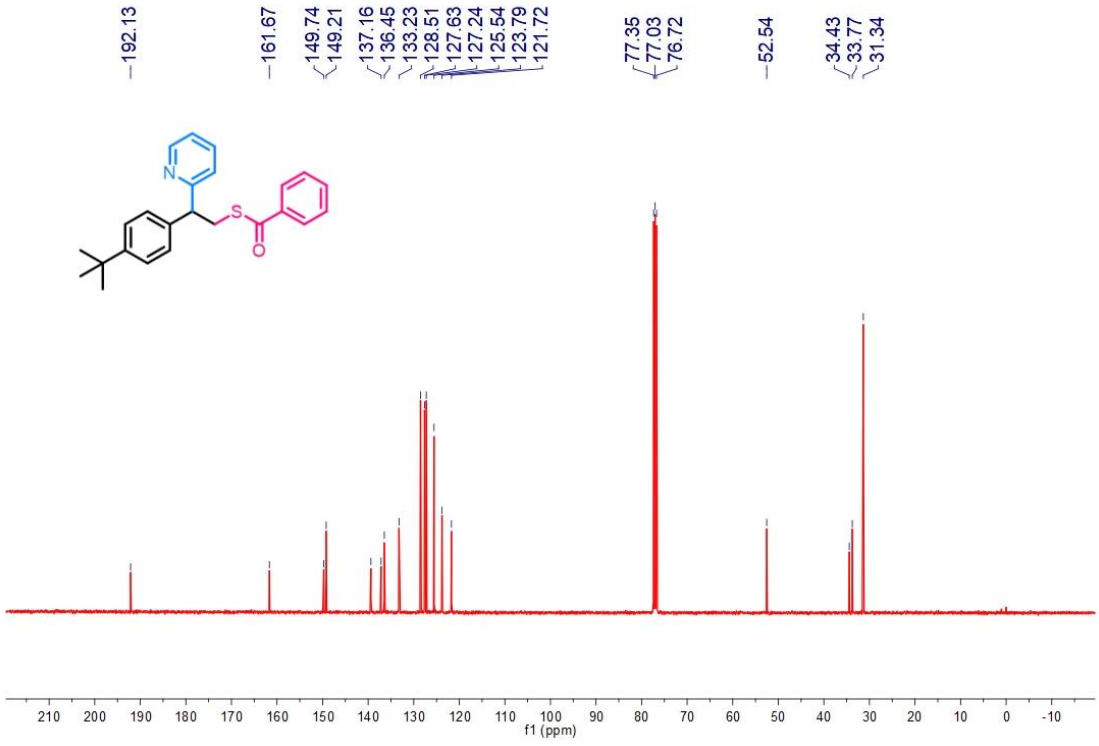


Fig. S27. The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for *S*-(2-(4-methoxyphenyl)-2-(pyridin-2-yl)ethyl) benzothioate (**3ad**) in $CDCl_3$

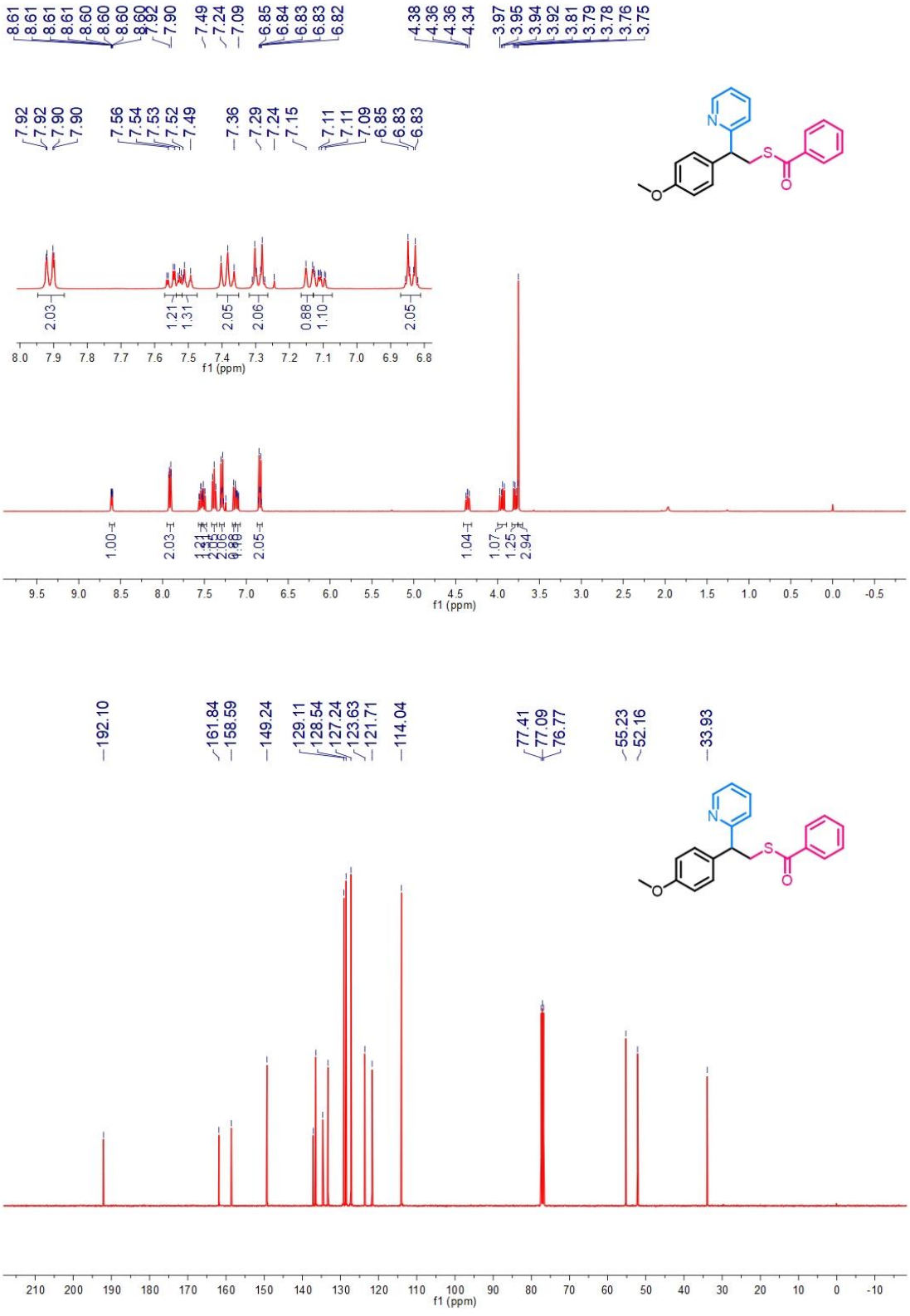
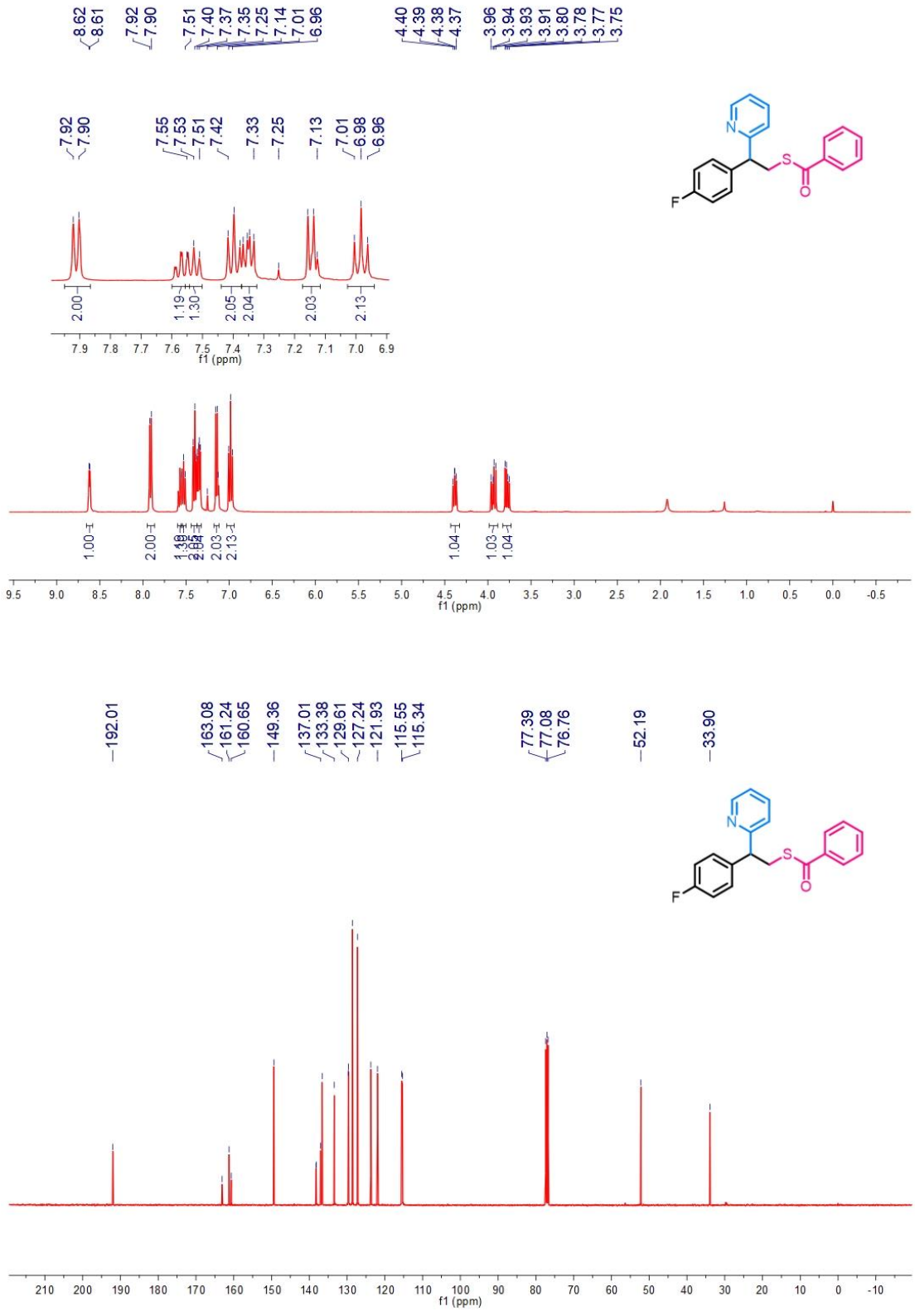


Fig. S28. The ^{1}H (400 MHz), ^{13}C (101 MHz) and ^{19}F (377 MHz) NMR spectra for *S*-(2-(4-fluorophenyl)-2-(pyridin-2-yl)ethyl) benzothioate (**3ae**) in $CDCl_3$



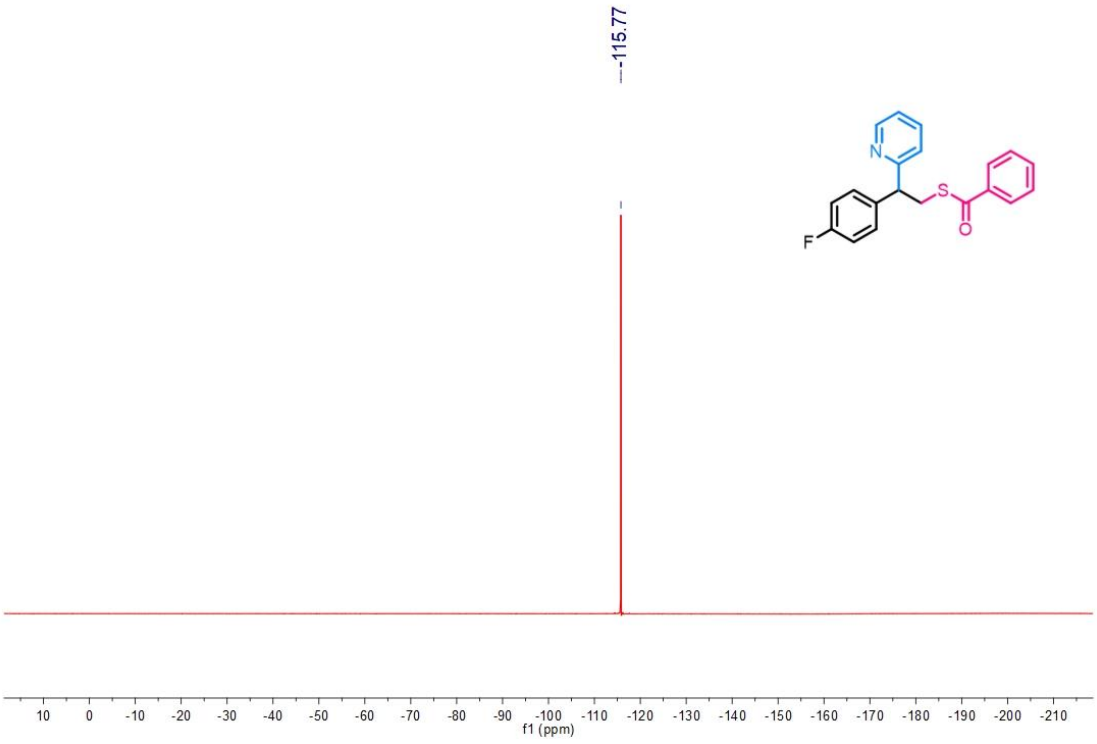

-115.77
N
S
O
F
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

Fig. S29. The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for *S*-(2-(4-chlorophenyl)-2-(pyridin-2-yl)ethyl) benzothioate (**3af**) in $CDCl_3$

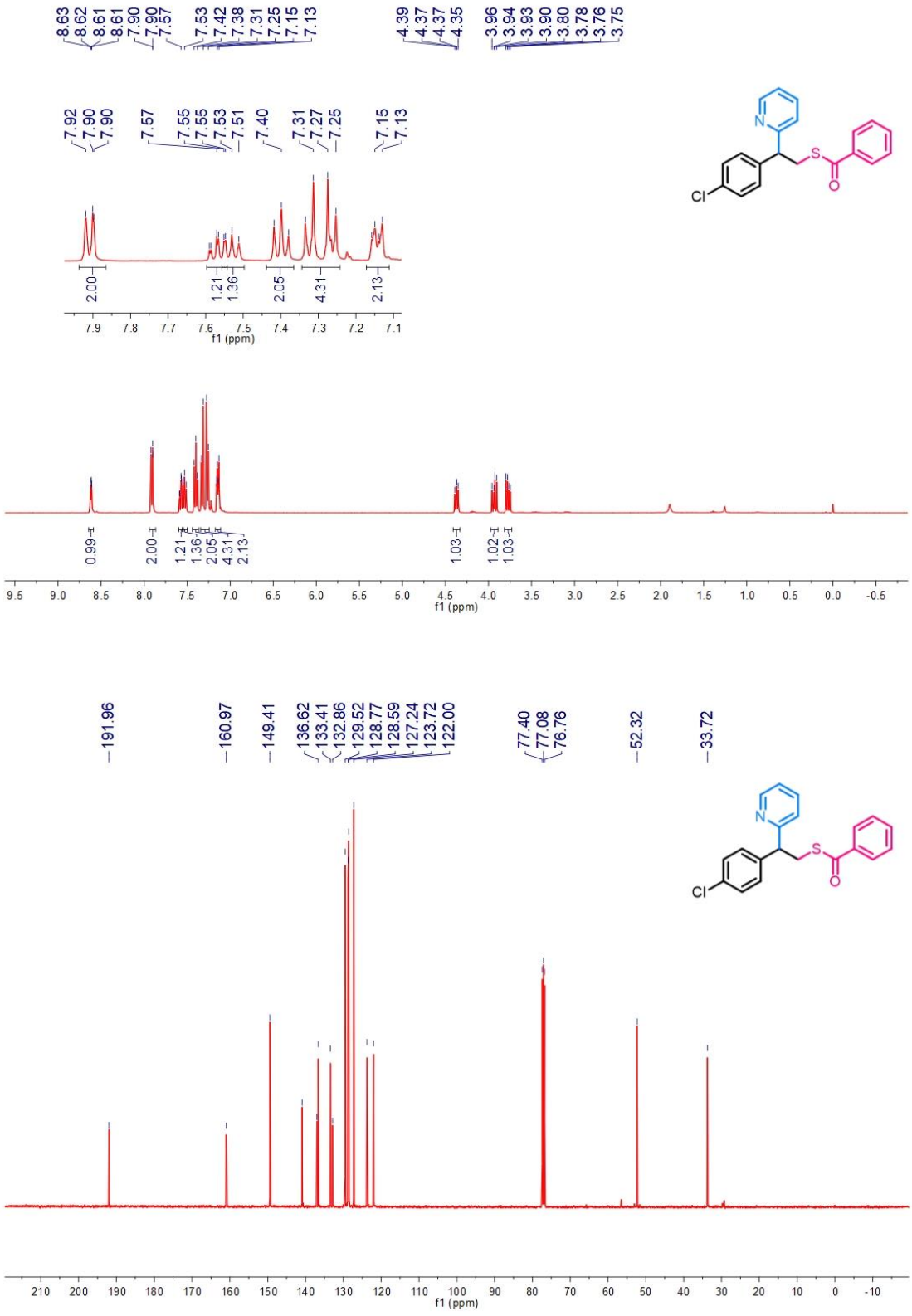


Fig. S30. The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for *S*-(2-(4-bromophenyl)-2-(pyridin-2-yl)ethyl) benzothioate (**3ag**) in $CDCl_3$

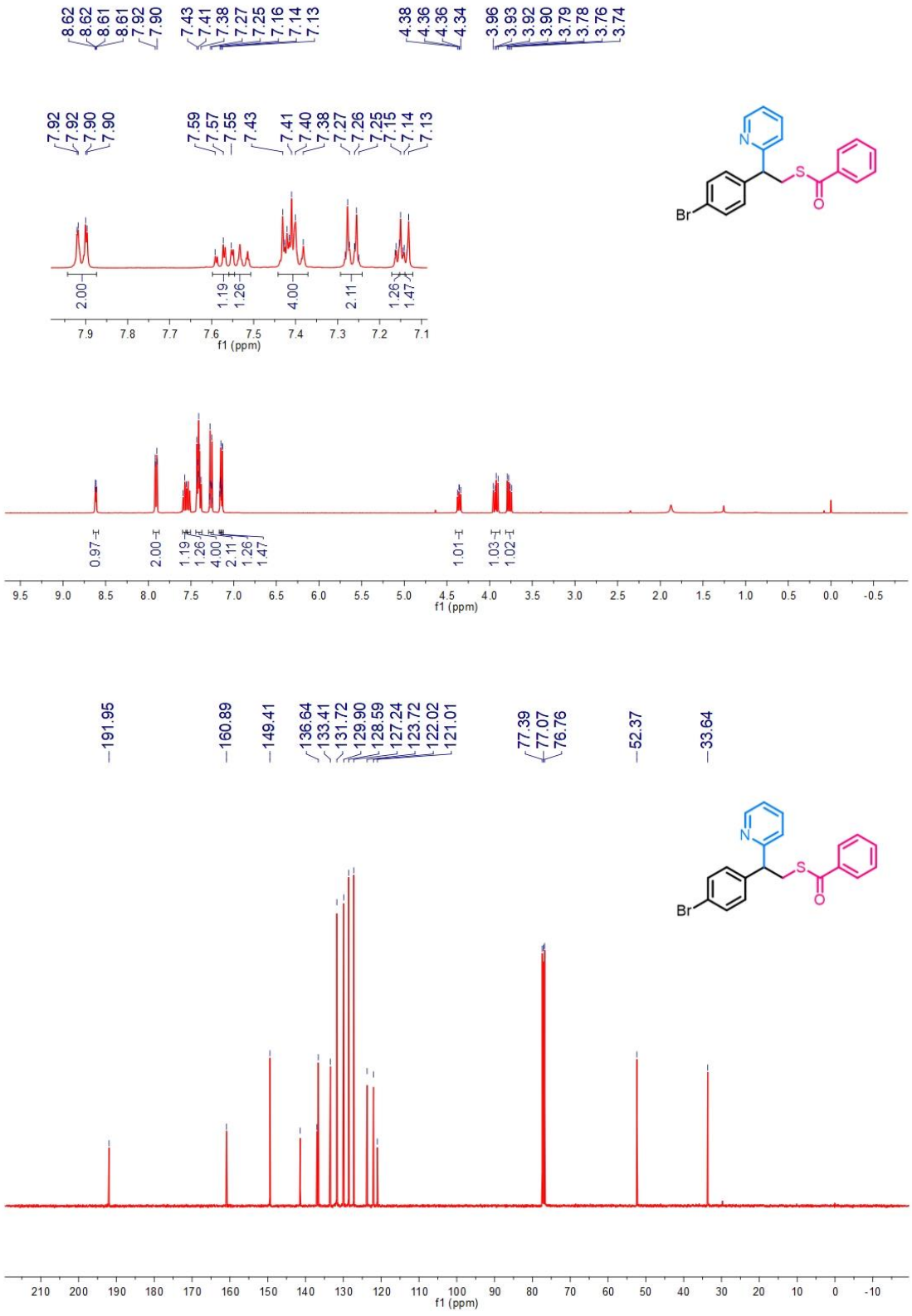
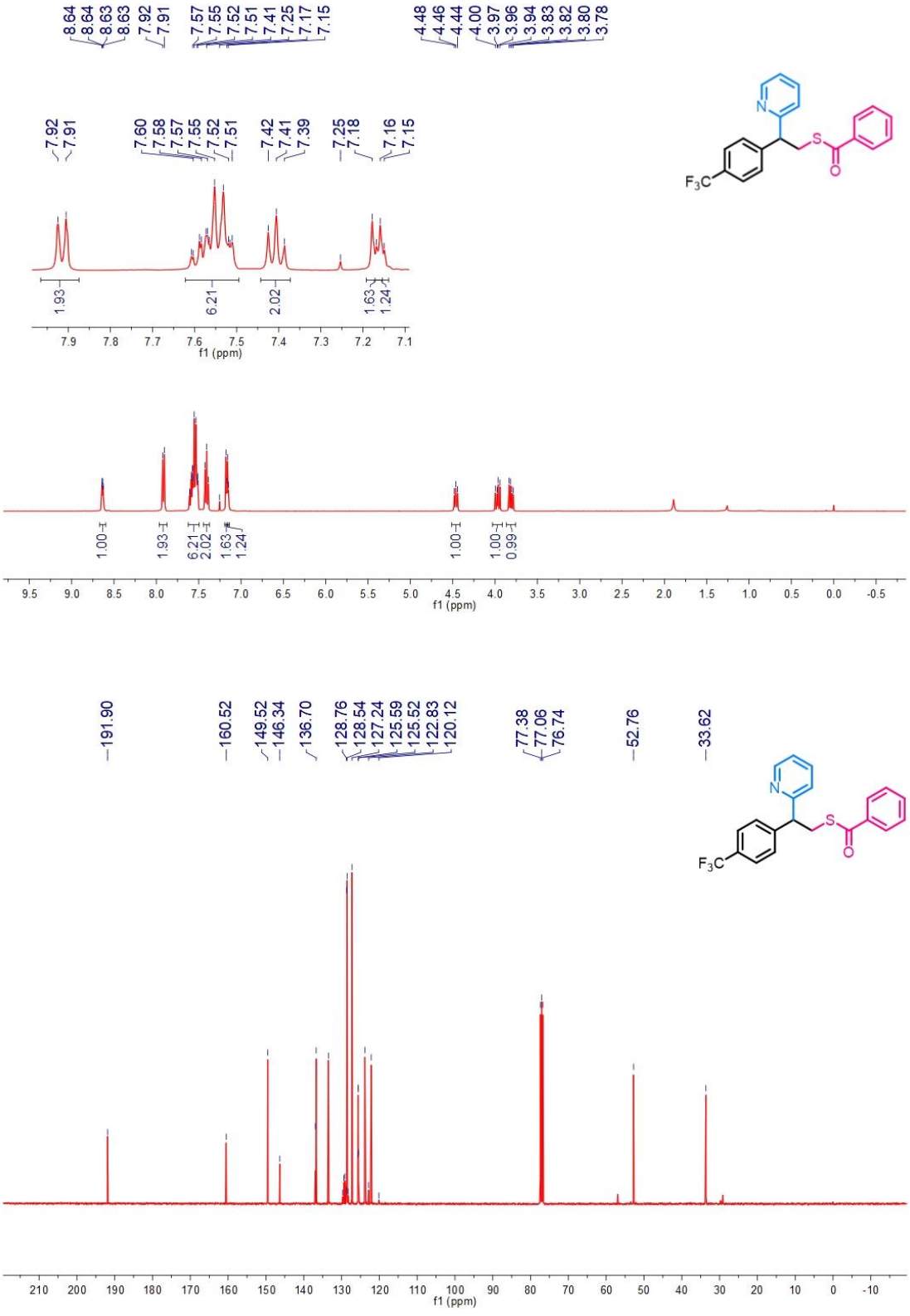


Fig. S31. The ^{1}H (400 MHz), ^{13}C (101 MHz) and ^{19}F (377 MHz) NMR spectra for *S*-(2-(pyridin-2-yl)-2-(4-(trifluoromethyl)phenyl)ethyl) benzothioate (**3ah**) in $CDCl_3$



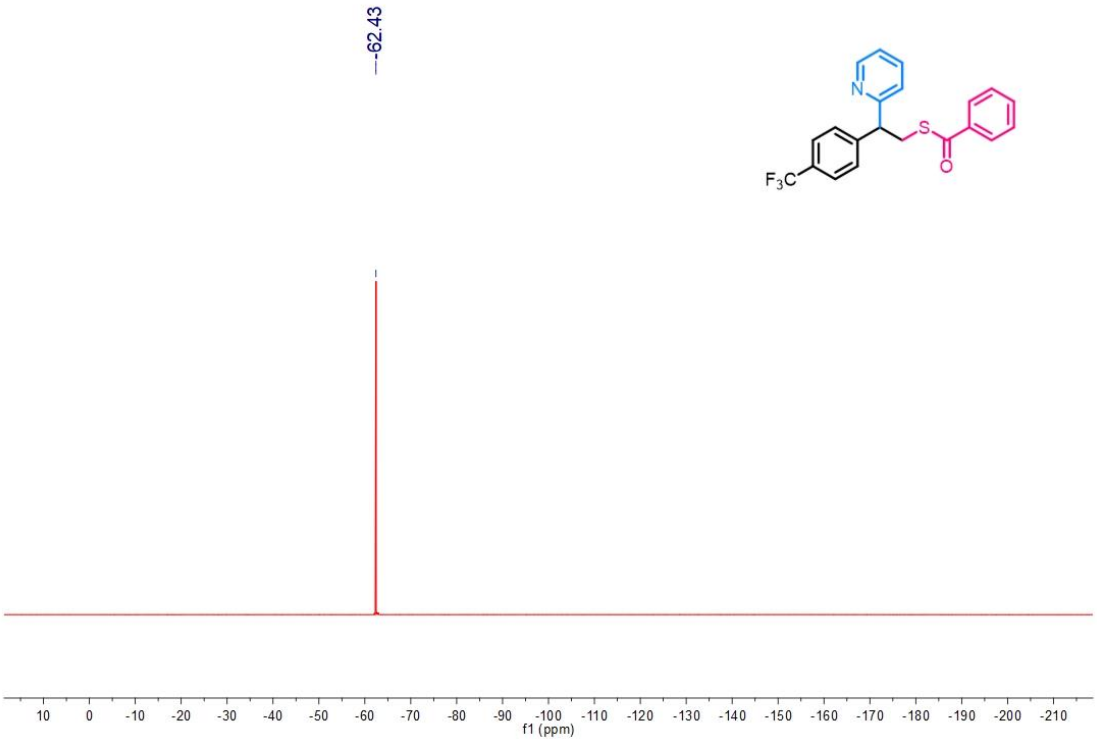

-62.43
N
S
O
F3C
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

Fig. S32. The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for 4-(2-(benzoylthio)-1-(pyridin-2-yl)ethyl)phenyl acetate (**3ai**) in $CDCl_3$

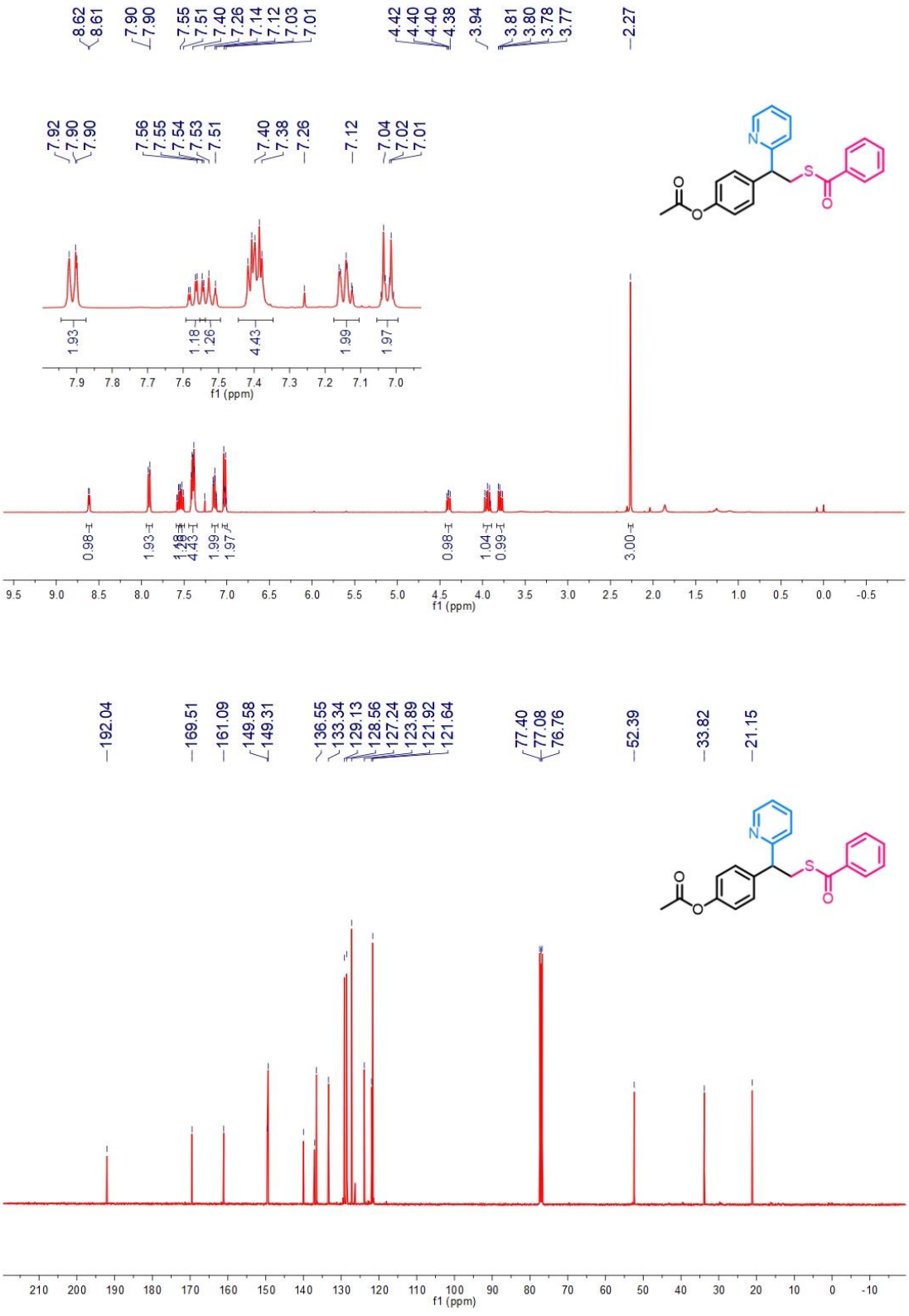


Fig. S33. The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for *S*-(2-(pyridin-2-yl)-2-(*m*-tolyl)ethyl) benzothioate (**3aj**) in $CDCl_3$

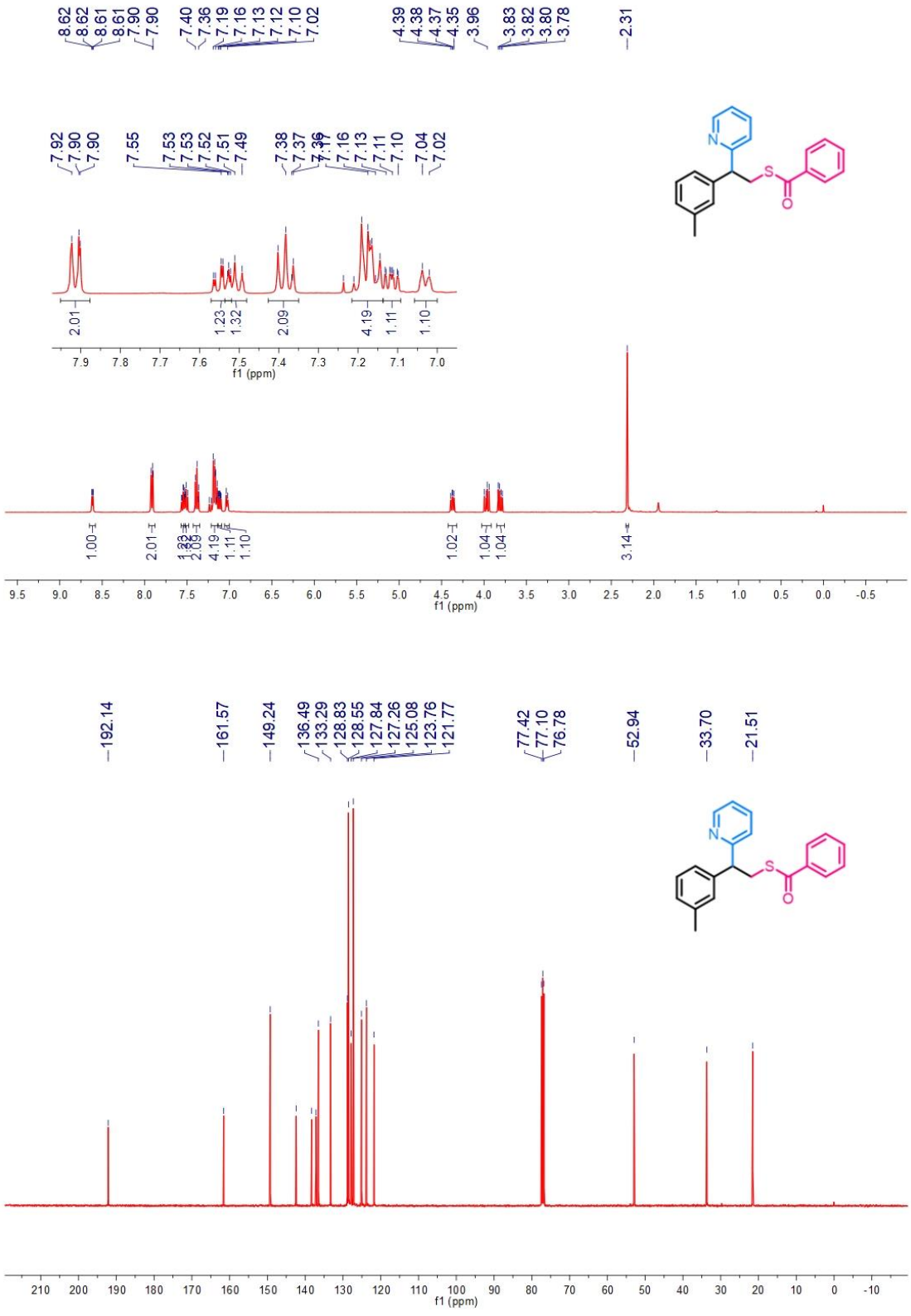


Fig. S34. The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for *S*-(2-(3-chlorophenyl)-2-(pyridin-2-yl)ethyl) benzothioate (**3ak**) in $CDCl_3$

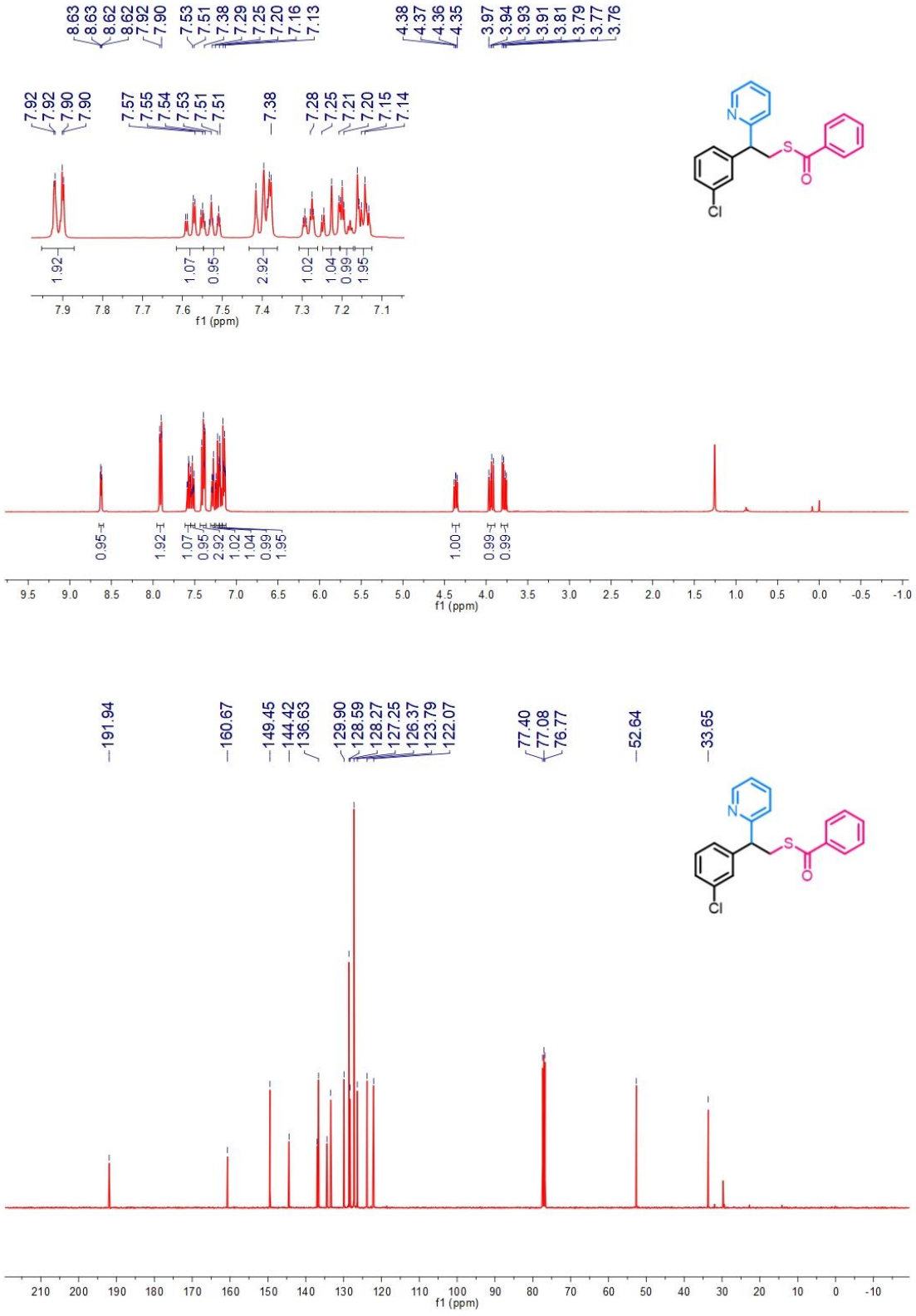


Fig. S35. The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for *S*-(2-(2-chlorophenyl)-2-(pyridin-2-yl)ethyl) benzothioate (**3al**) in $CDCl_3$

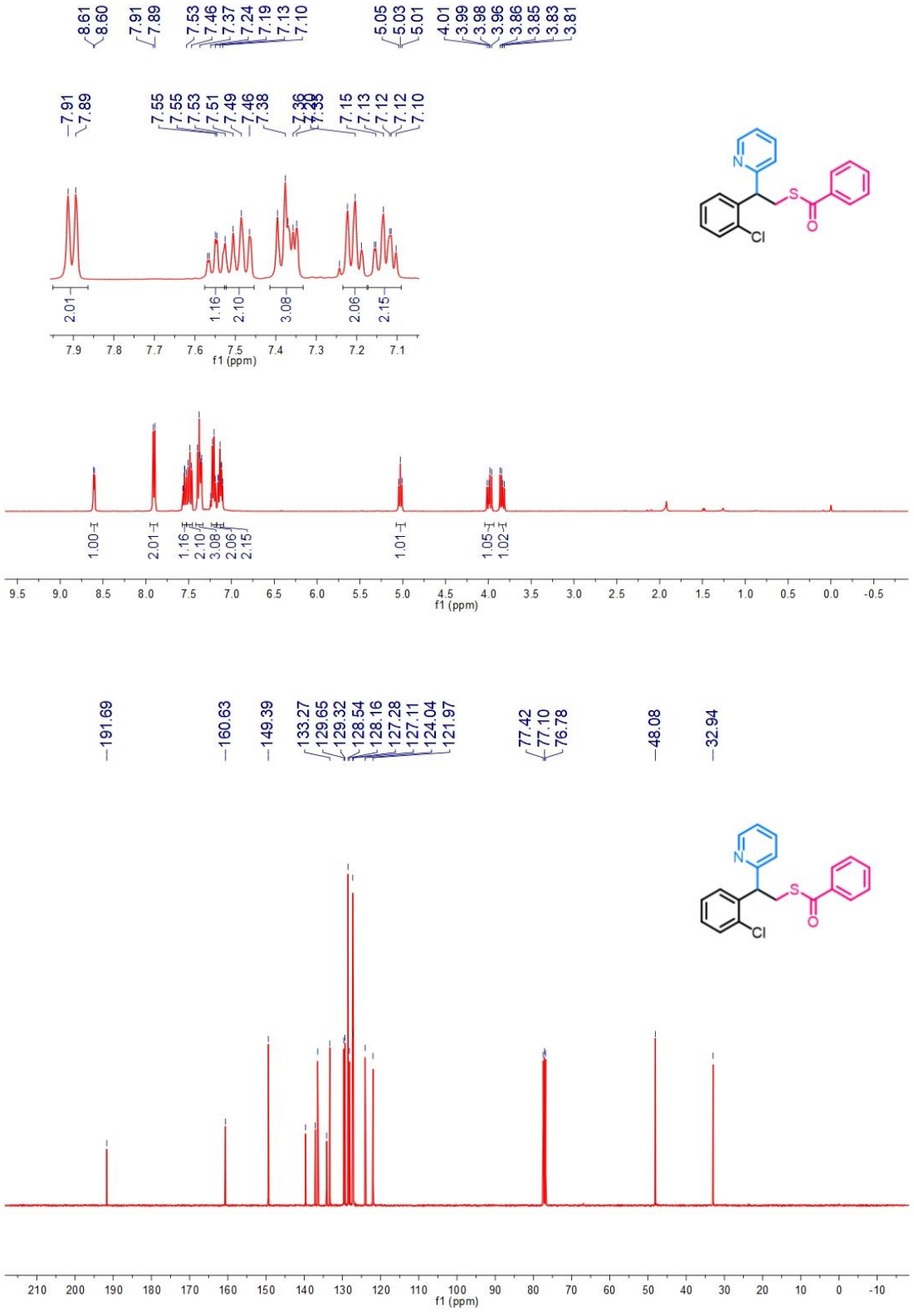


Fig. S36. The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for *S*-(2-(naphthalen-2-yl)-2-(pyridin-2-yl)ethyl) benzothioate (**3am**) in $CDCl_3$

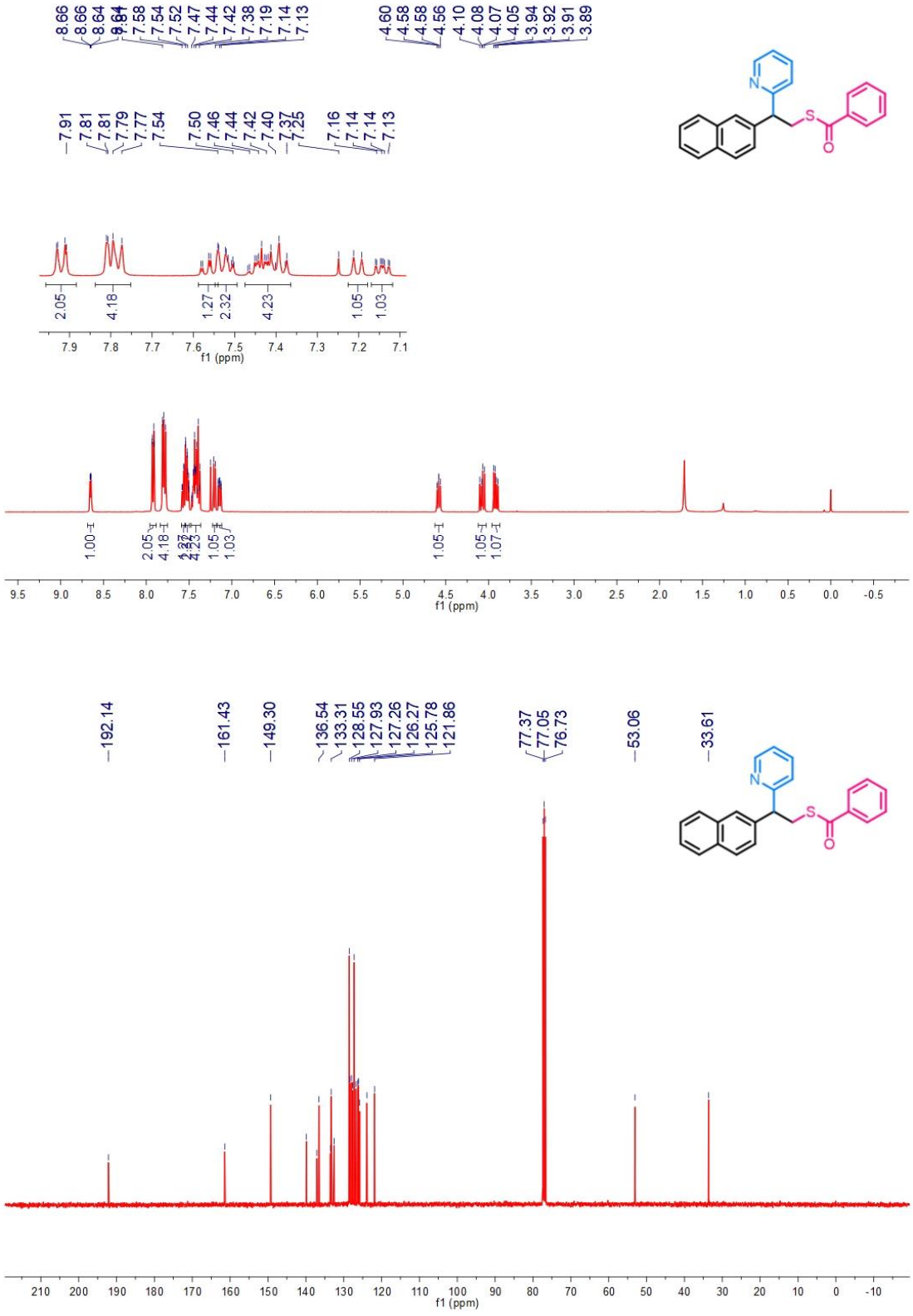


Fig. S37. The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for *S*-(2,2-di(pyridin-2-yl)ethyl) benzothioate (**3an**) in $CDCl_3$

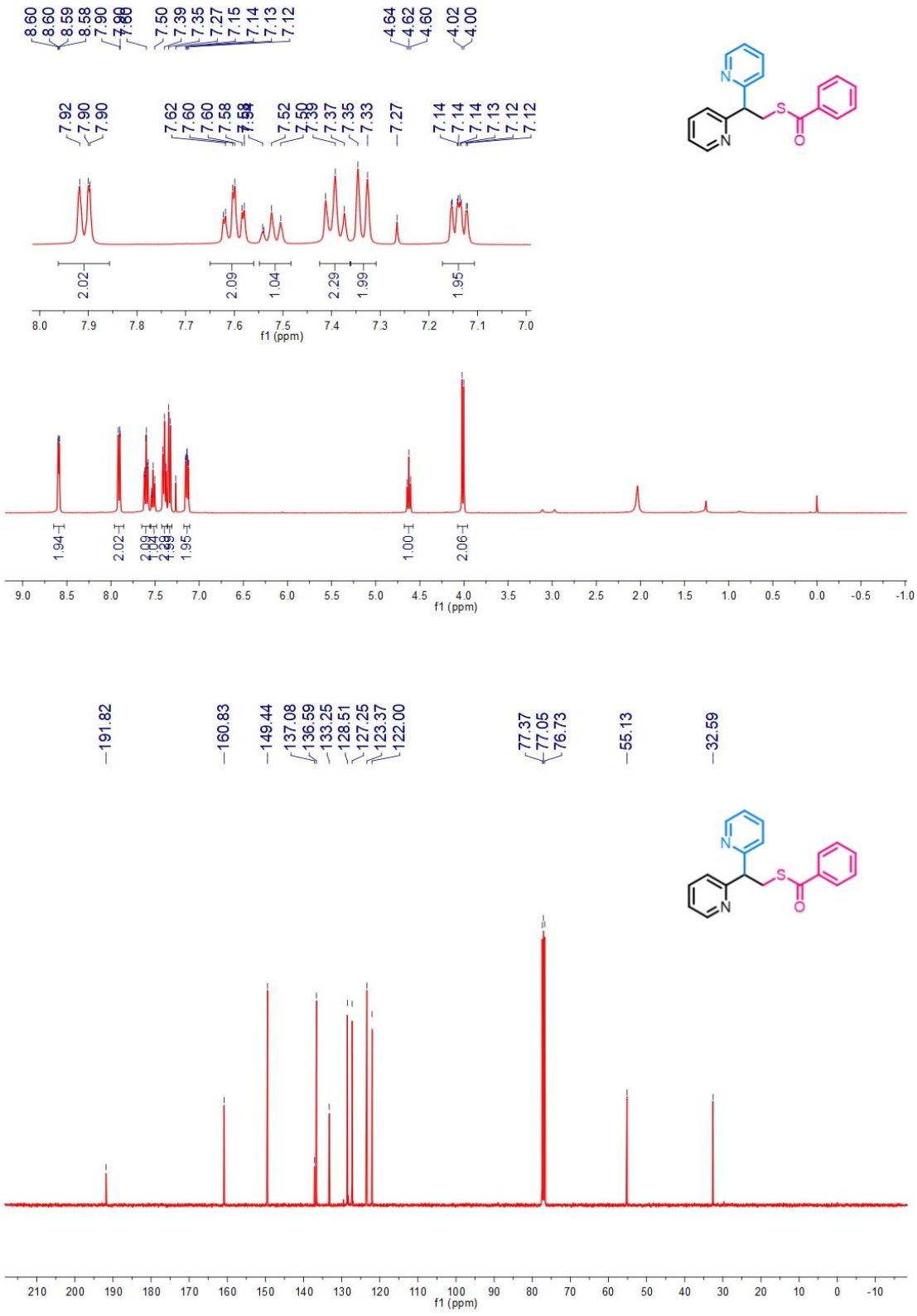


Fig. S38. The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for *S*-(2-phenyl-2-(pyridin-2-yl)propyl) benzothioate (**3ao**) in $CDCl_3$

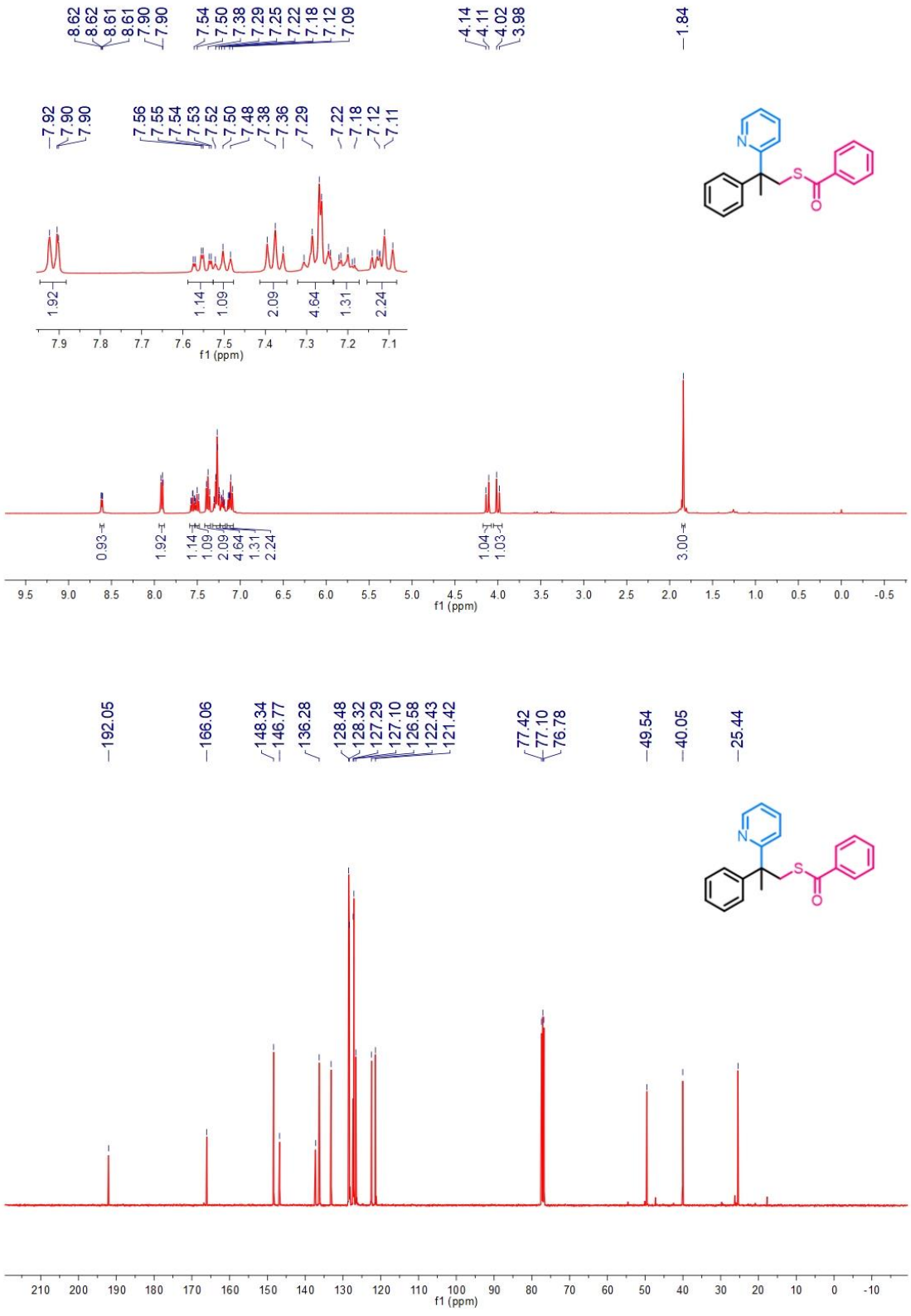


Fig. S39. The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for *S*-(2,2-diphenyl-2-(pyridin-2-yl)ethyl) benzothioate (**3ap**) in $CDCl_3$

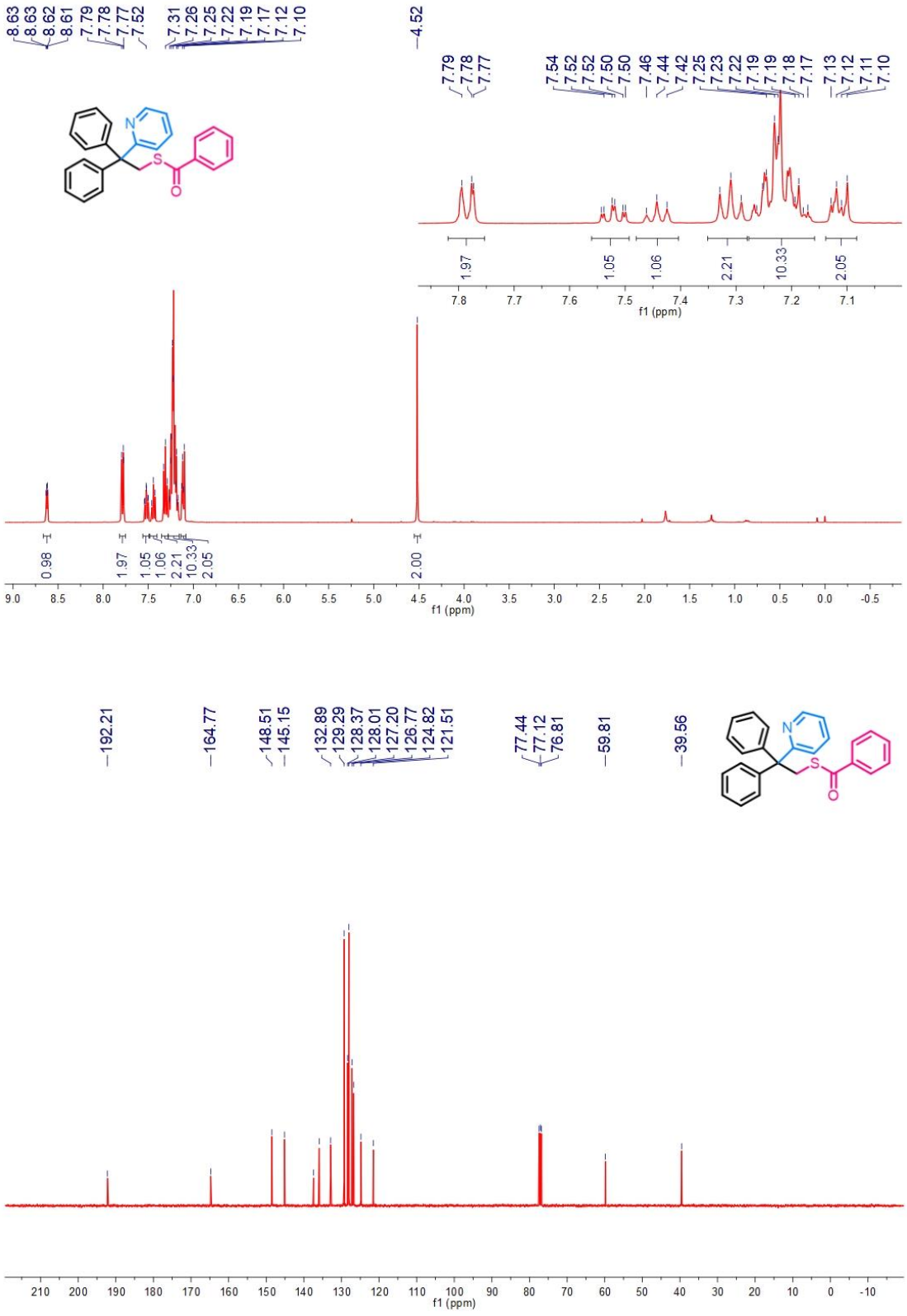


Fig. S40. The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for *S*-(1-phenyl-1-(pyridin-2-yl)propan-2-yl) benzothioate (**3aq**) in $CDCl_3$

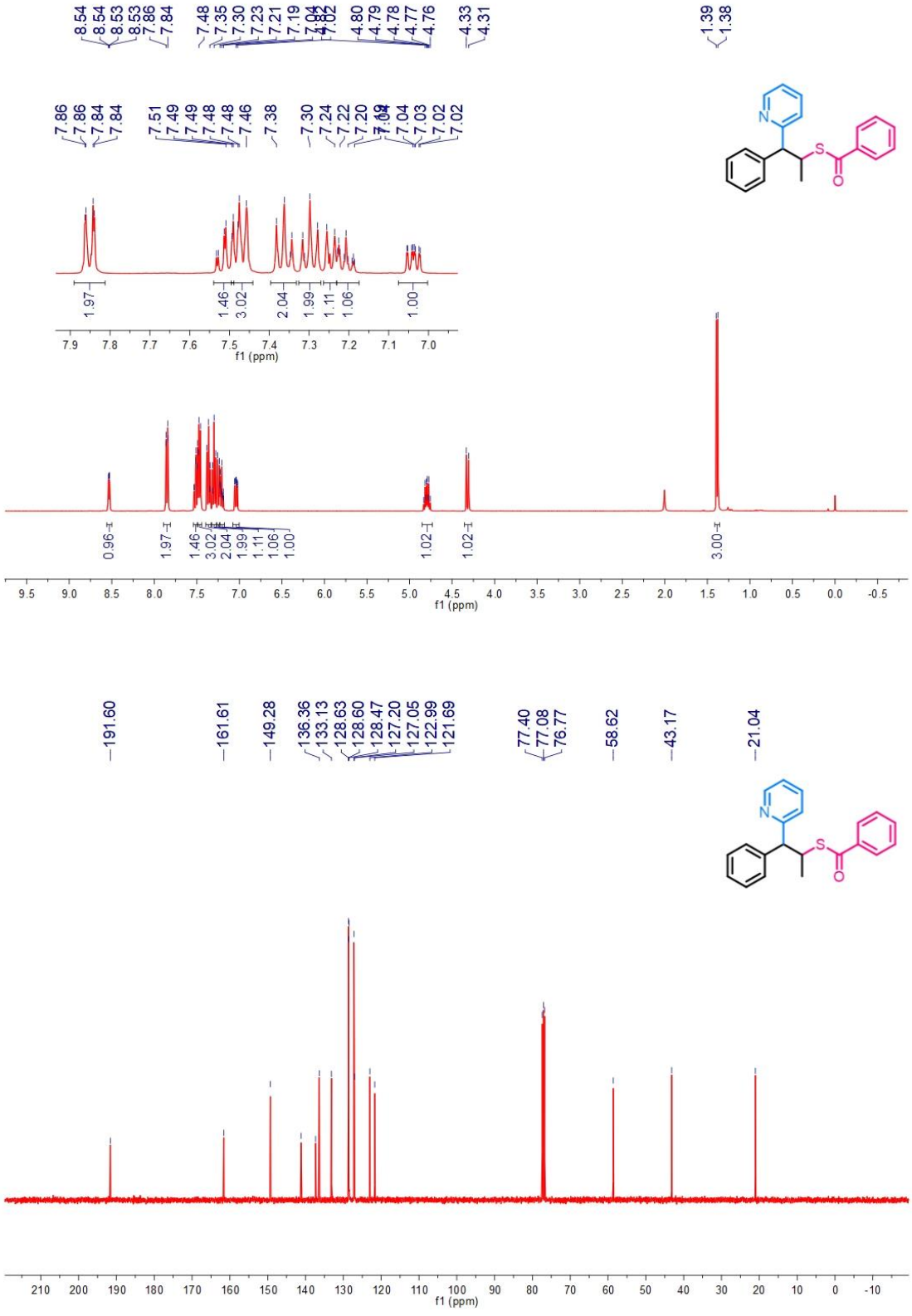


Fig. S41. The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for *S*-(3-phenyl-2-(pyridin-2-yl)propyl) benzothioate (**3ar**) in $CDCl_3$

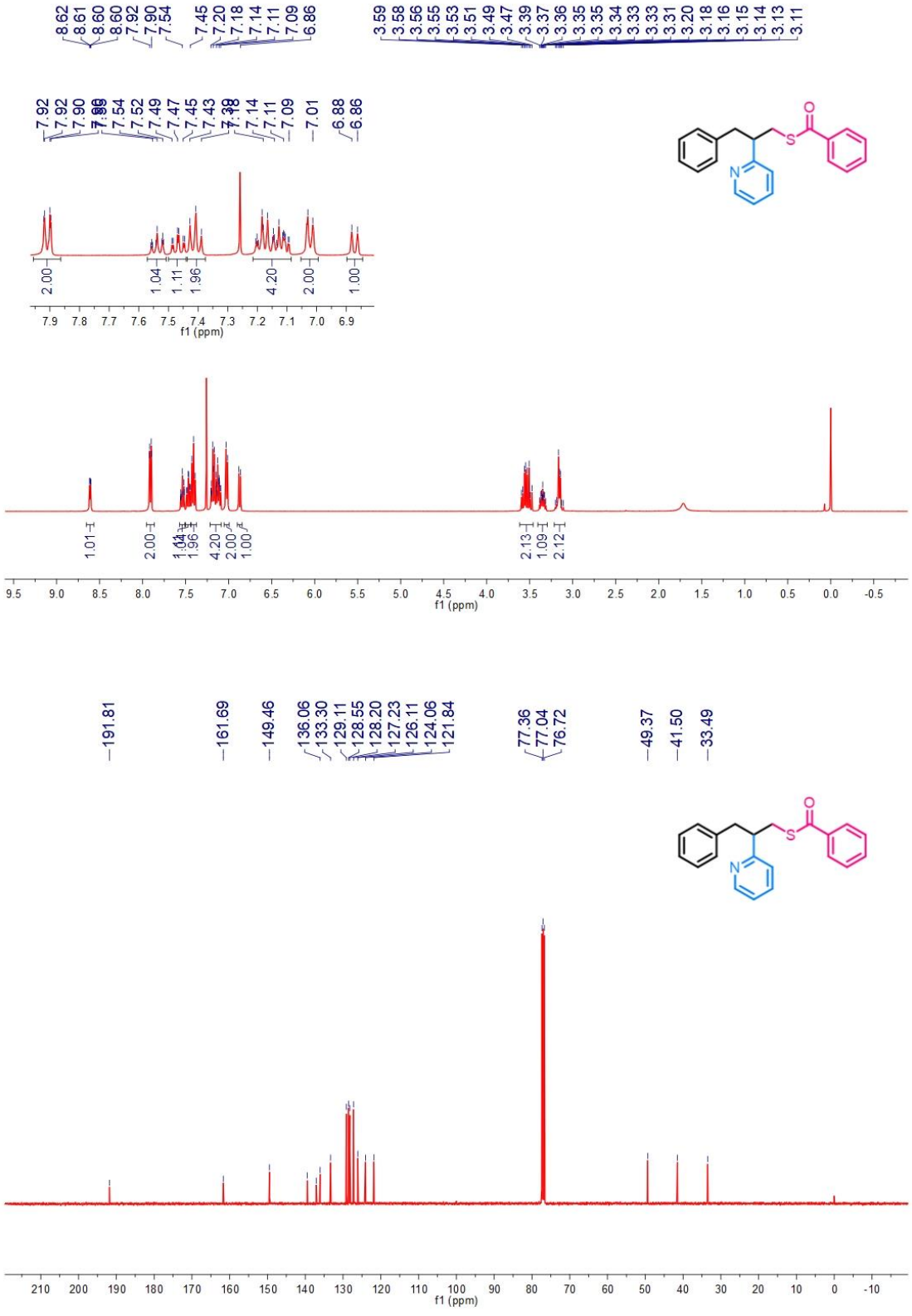
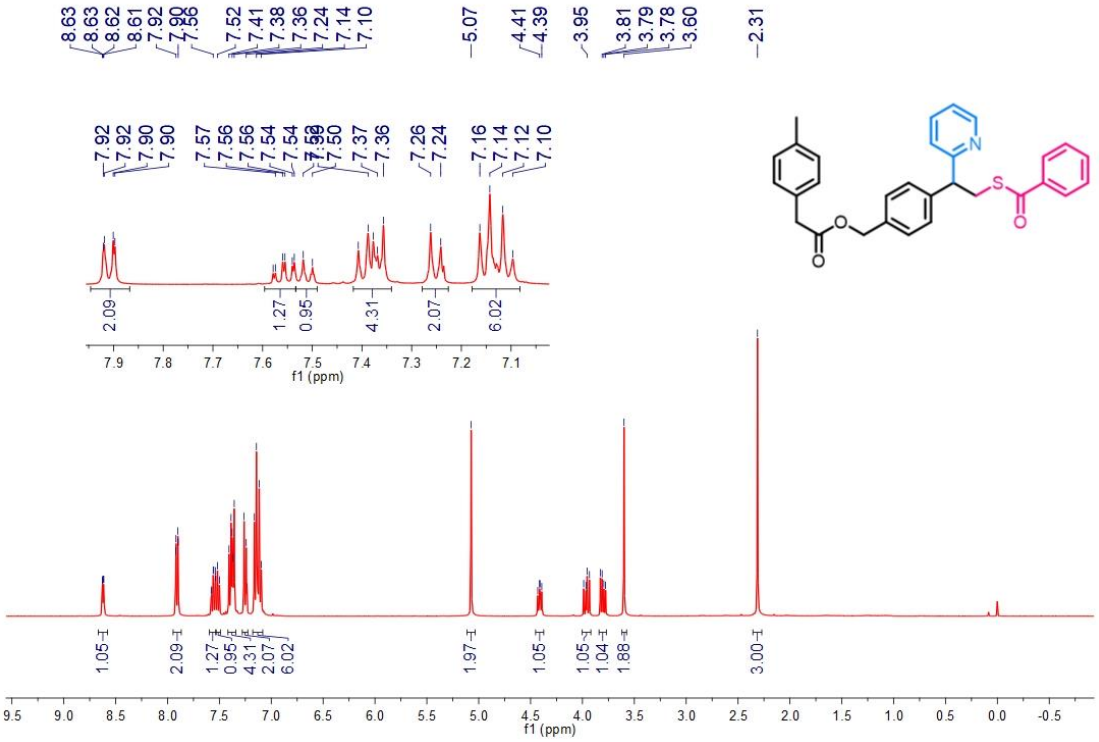


Fig. S42. The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for 4-(2-(benzoylthio)-1-(pyridin-2-yl)ethyl)benzyl 2-(*p*-tolyl)acetate (**3as**) in $CDCl_3$



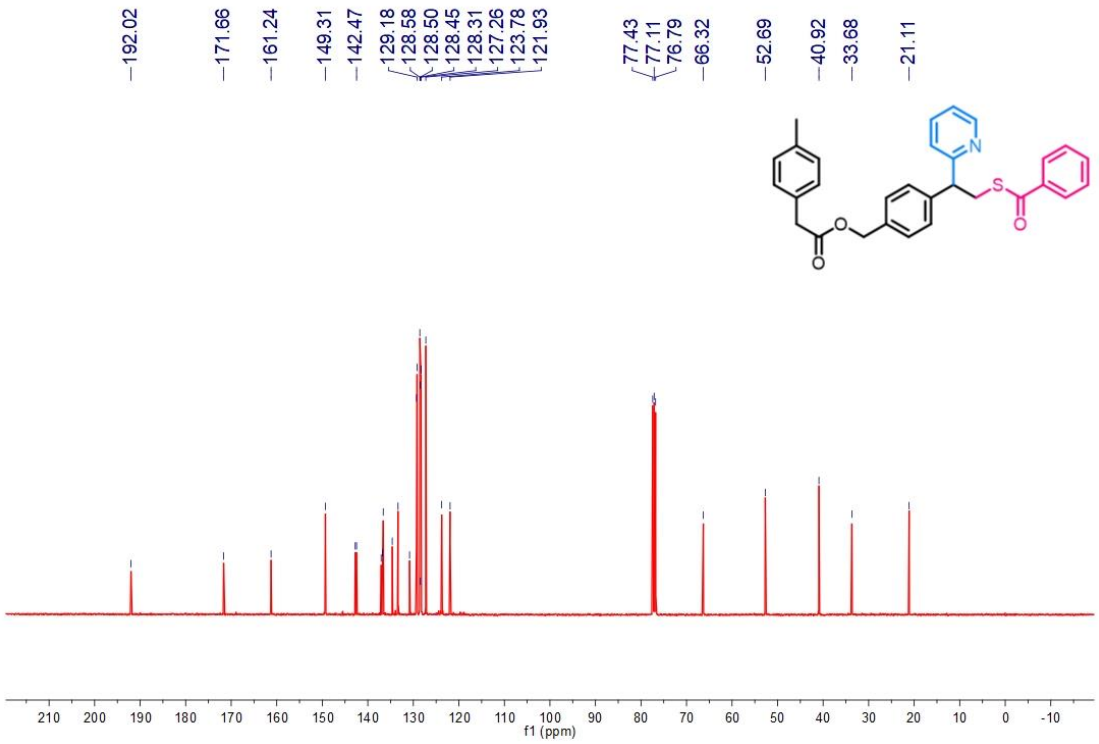


Fig. S43. The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for 4-(2-(benzoylthio)-1-(pyridin-2-yl)ethyl)benzyl 2-(1-methyl-5-(4-methylbenzoyl)-1H-pyrrol-2-yl)acetate (**3at**) in $CDCl_3$

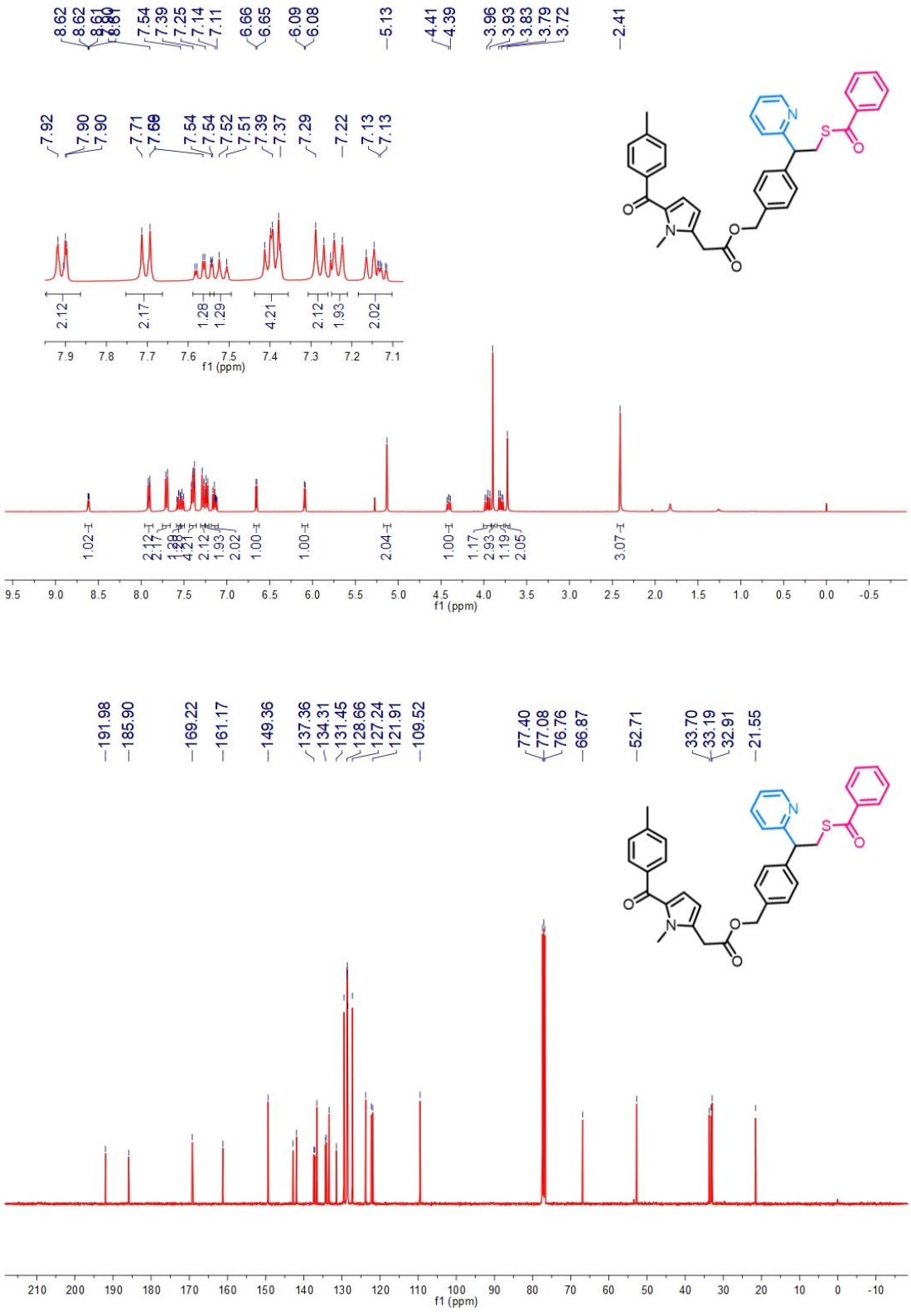
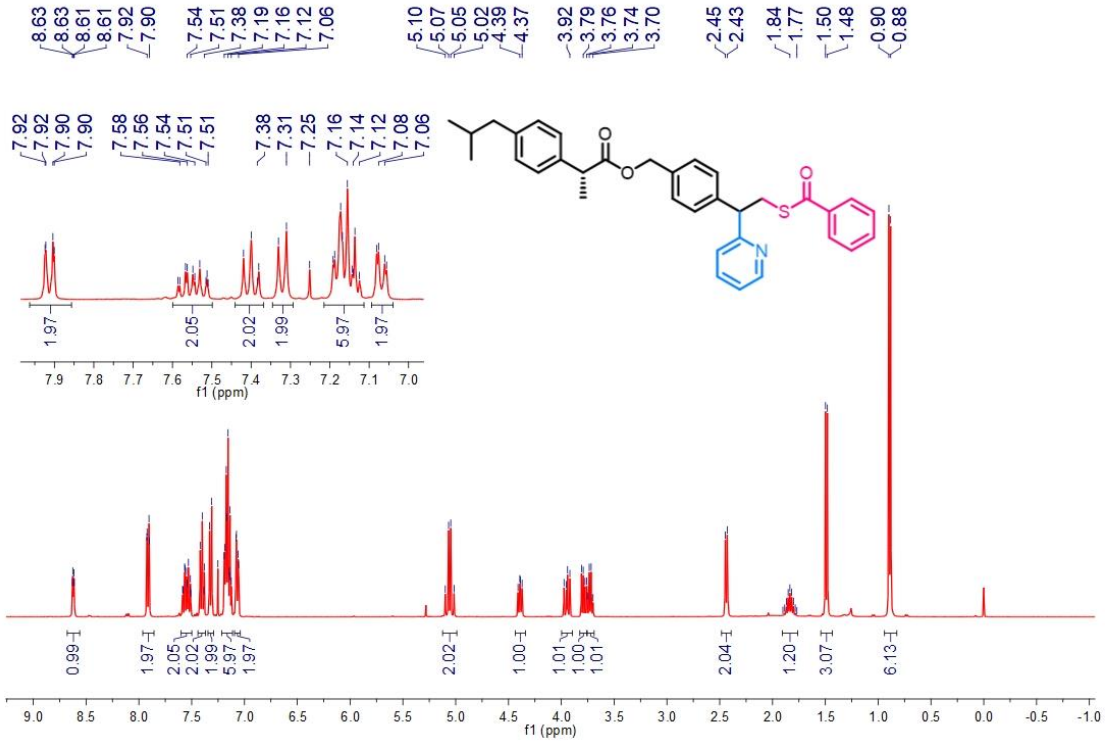


Fig. S44. The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for 4-(2-(benzoylthio)-1-(pyridin-2-yl)ethyl)benzyl (2*R*)-2-(4-isobutylphenyl)propanoate (**3au**) in $CDCl_3$



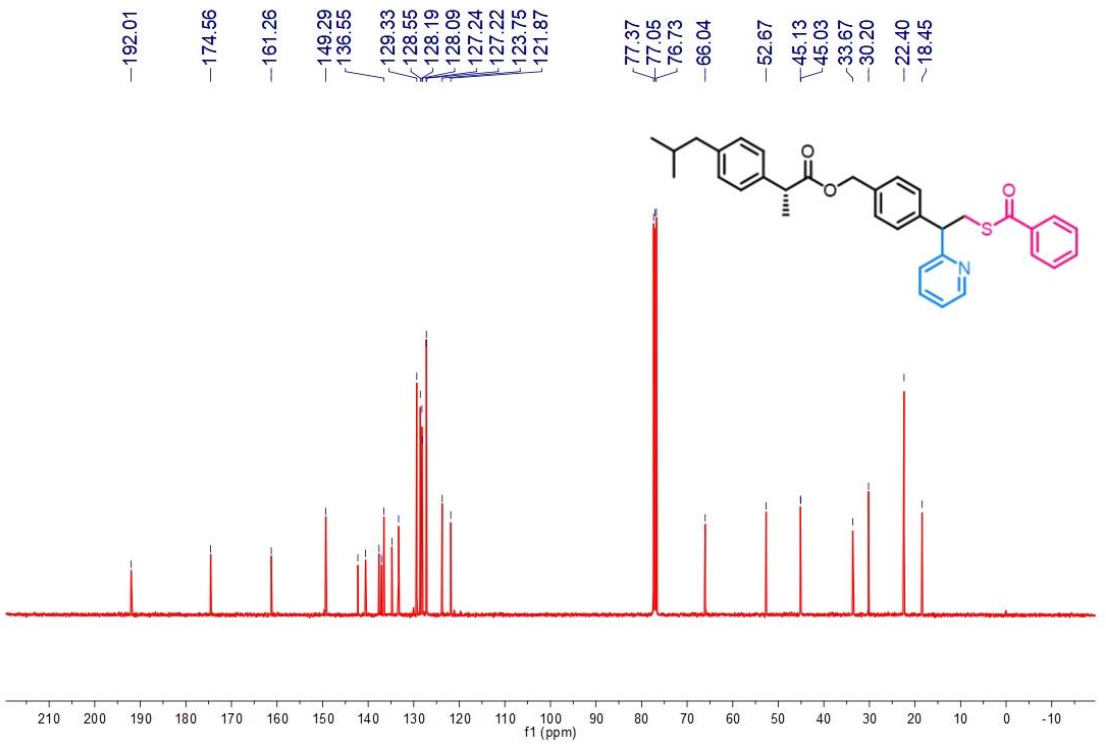


Fig. S45. The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for 4-(2-(benzoylthio)-1-(pyridin-2-yl)ethyl)benzyl (2*S*)-2-(6-methoxynaphthalen-2-yl)propanoate (**3av**) in $CDCl_3$

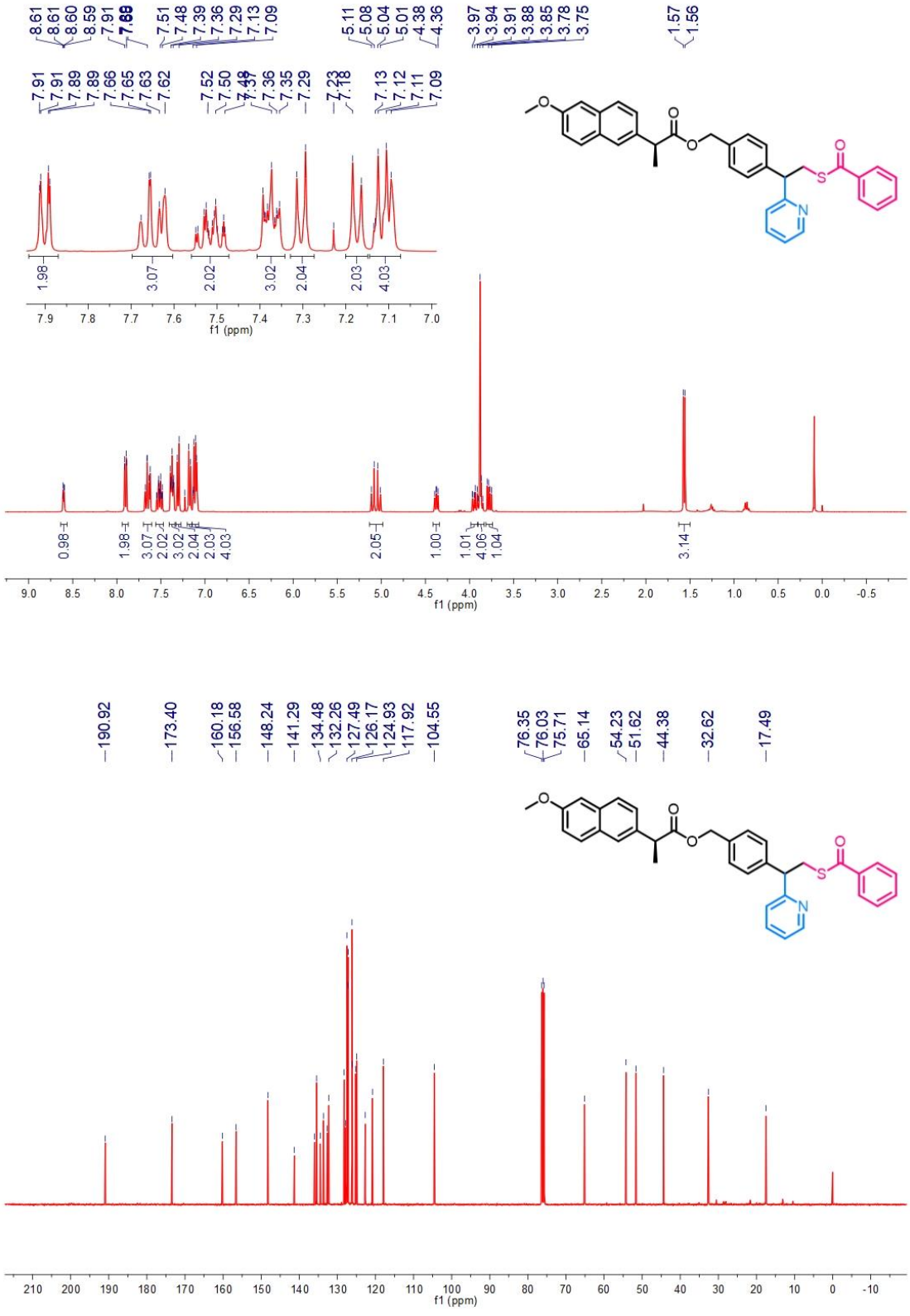


Fig. S46. The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for *S*-(1-cyclopropyl-2-phenyl-2-(pyridin-2-yl)ethyl) benzothioate (**3aw**) in $CDCl_3$

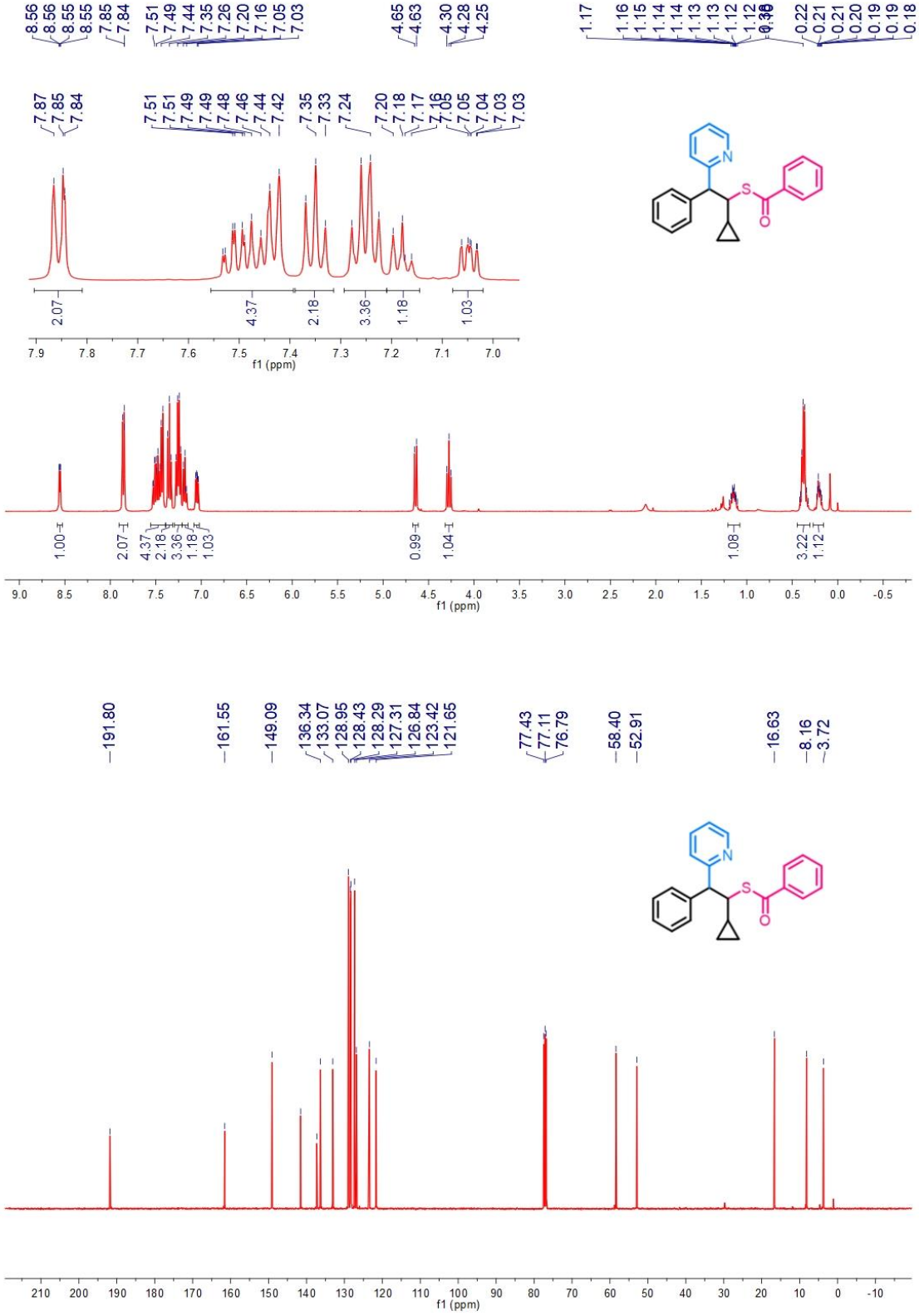


Fig. S47. The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for *S*-(2-cyclopropyl-2-phenyl-2-(pyridin-2-yl)ethyl) benzothioate (**3ax**) in $CDCl_3$

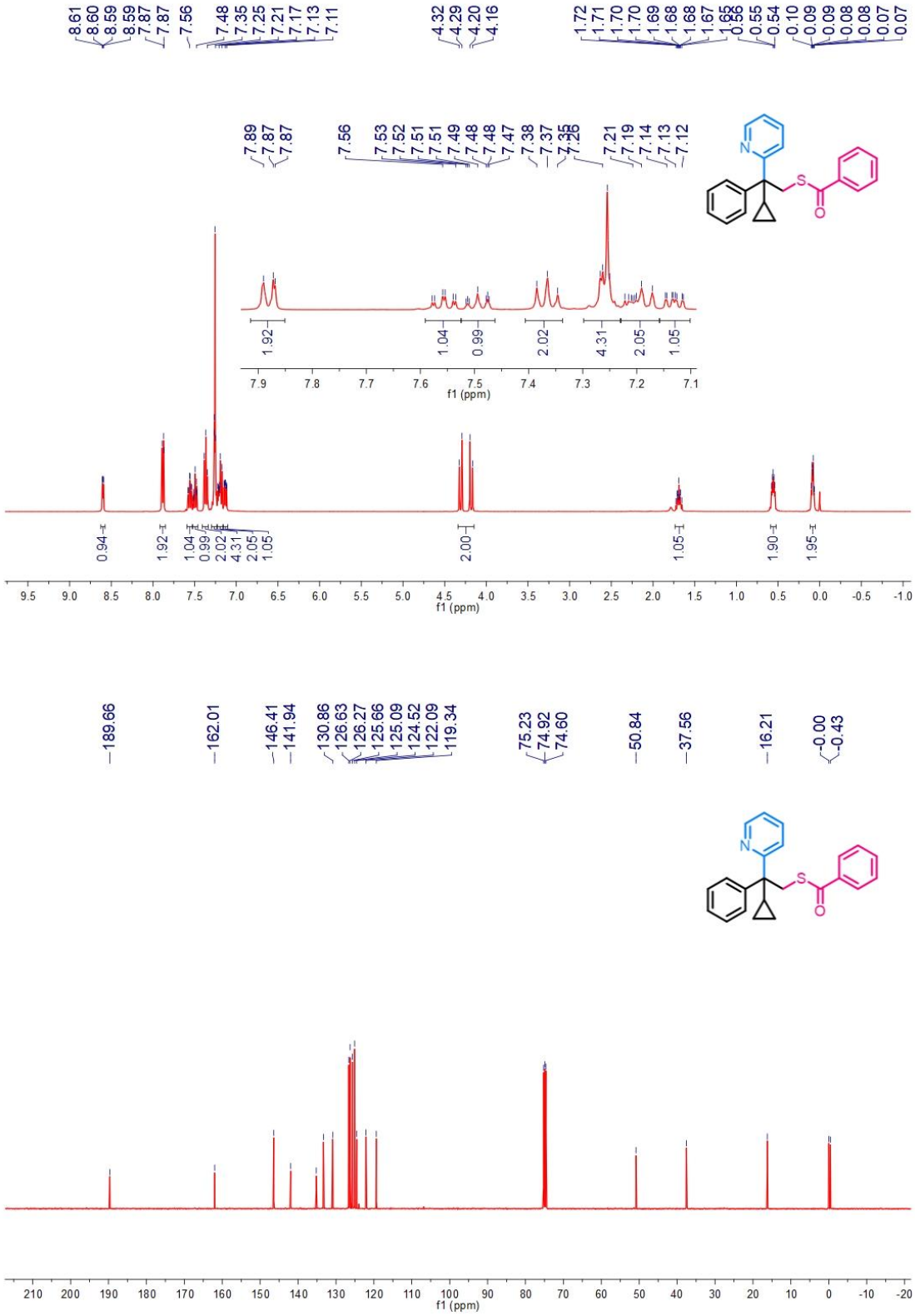


Fig. S48. The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for *S*-(2-(pyridin-2-yl)-2-(2-vinylphenyl)ethyl) benzothioate (**3ay**) in $CDCl_3$

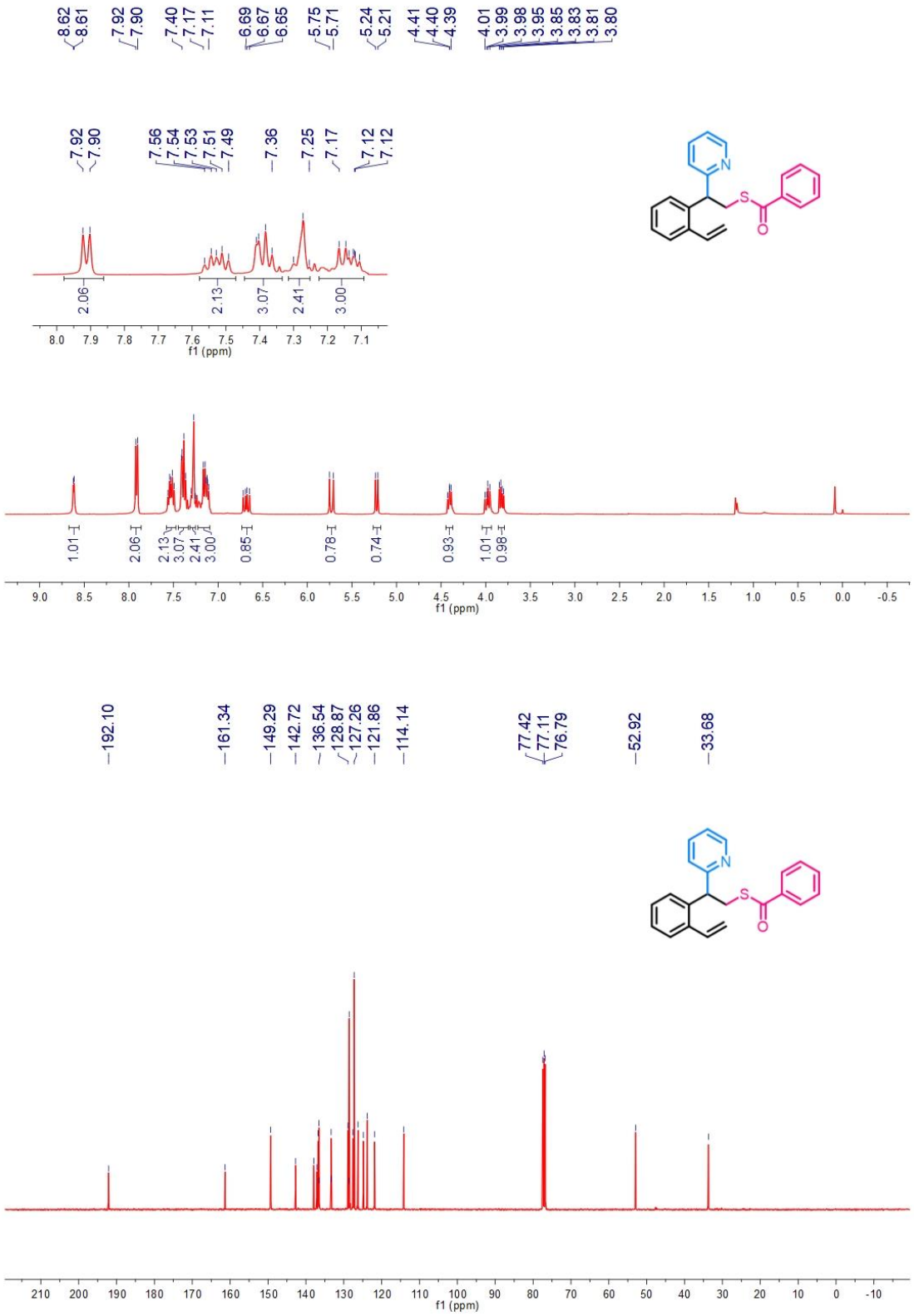


Fig. S49. The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for *S*-(2-phenyl-2-(pyridin-2-yl)ethyl) 4-methylbenzothioate (**3ba**) in $CDCl_3$

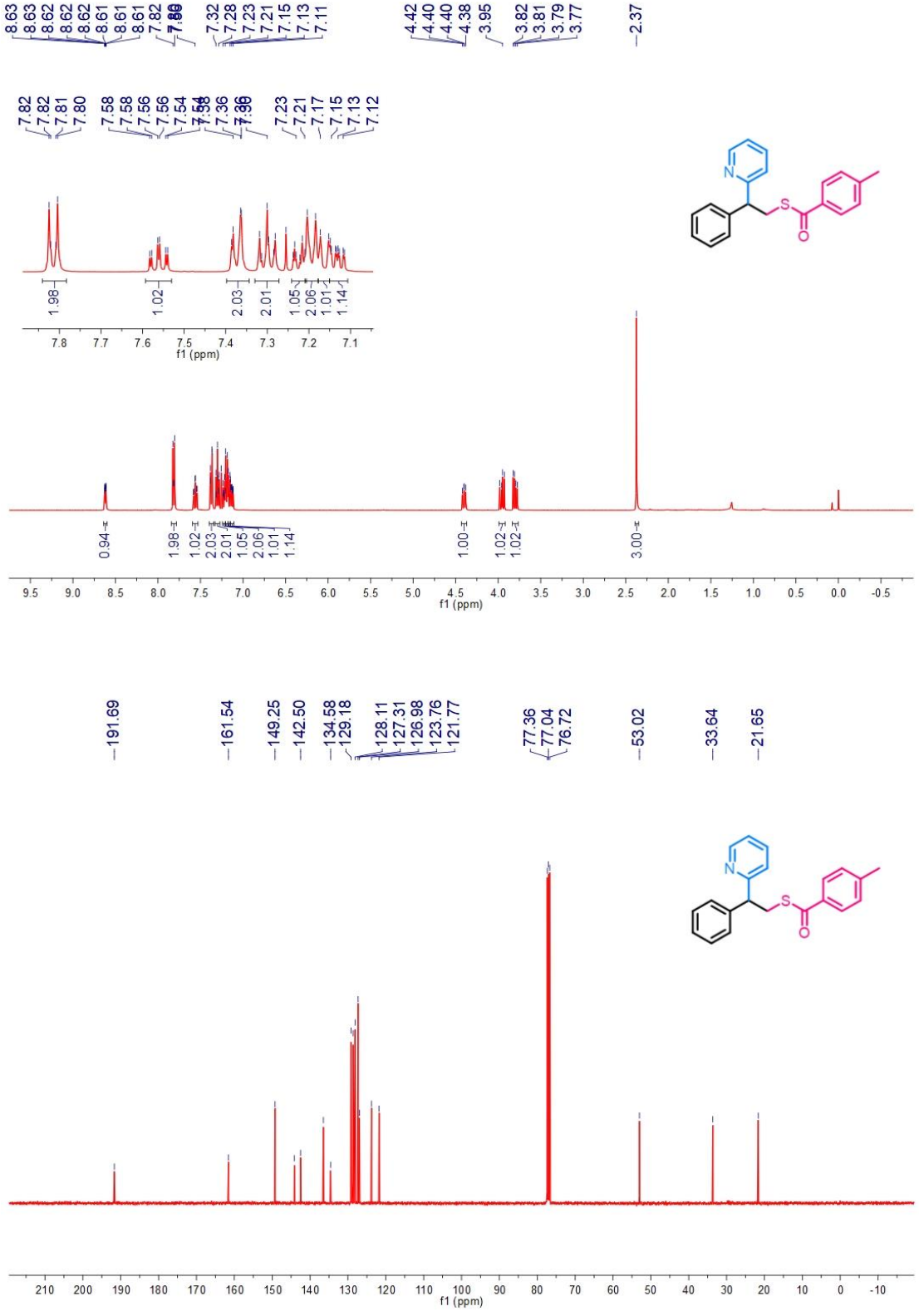


Fig. S50. The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for *S*-(2-phenyl-2-(pyridin-2-yl)ethyl) 4-methoxybenzothioate (**3ca**) in $CDCl_3$

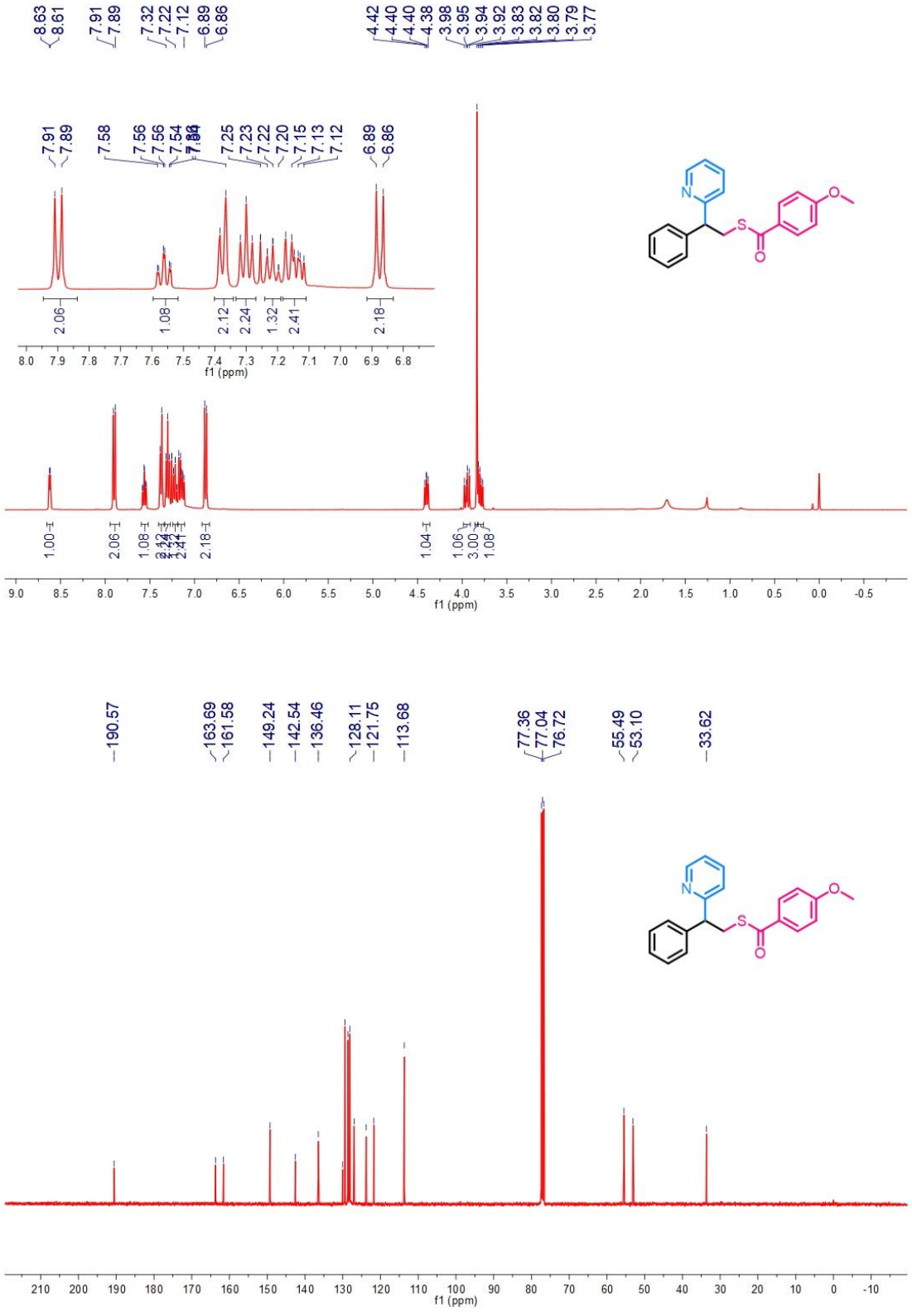


Fig. S51. The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for *S*-(2-phenyl-2-(pyridin-2-yl)ethyl) 4-(*tert*-butyl)benzothioate (**3da**) in $CDCl_3$

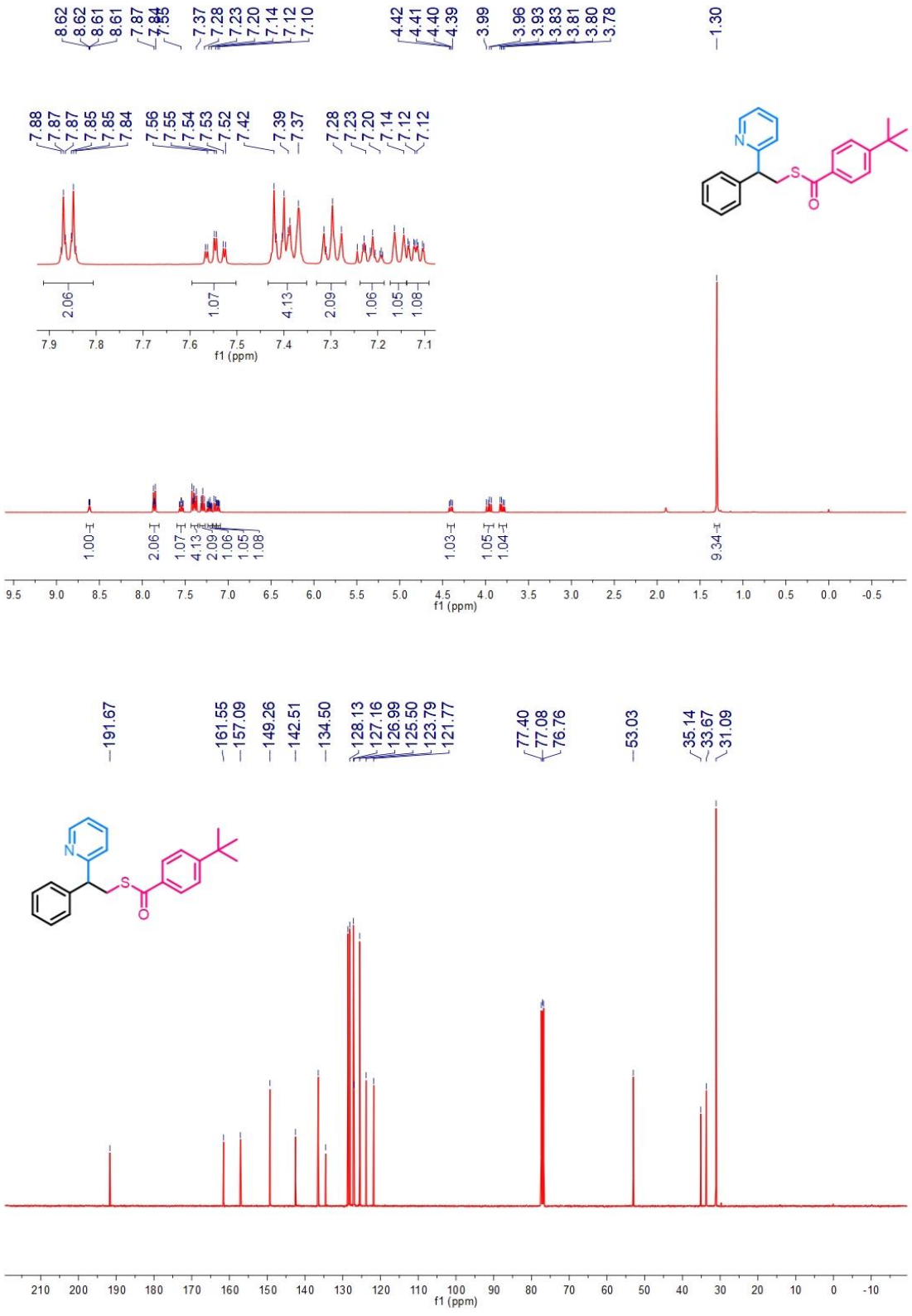
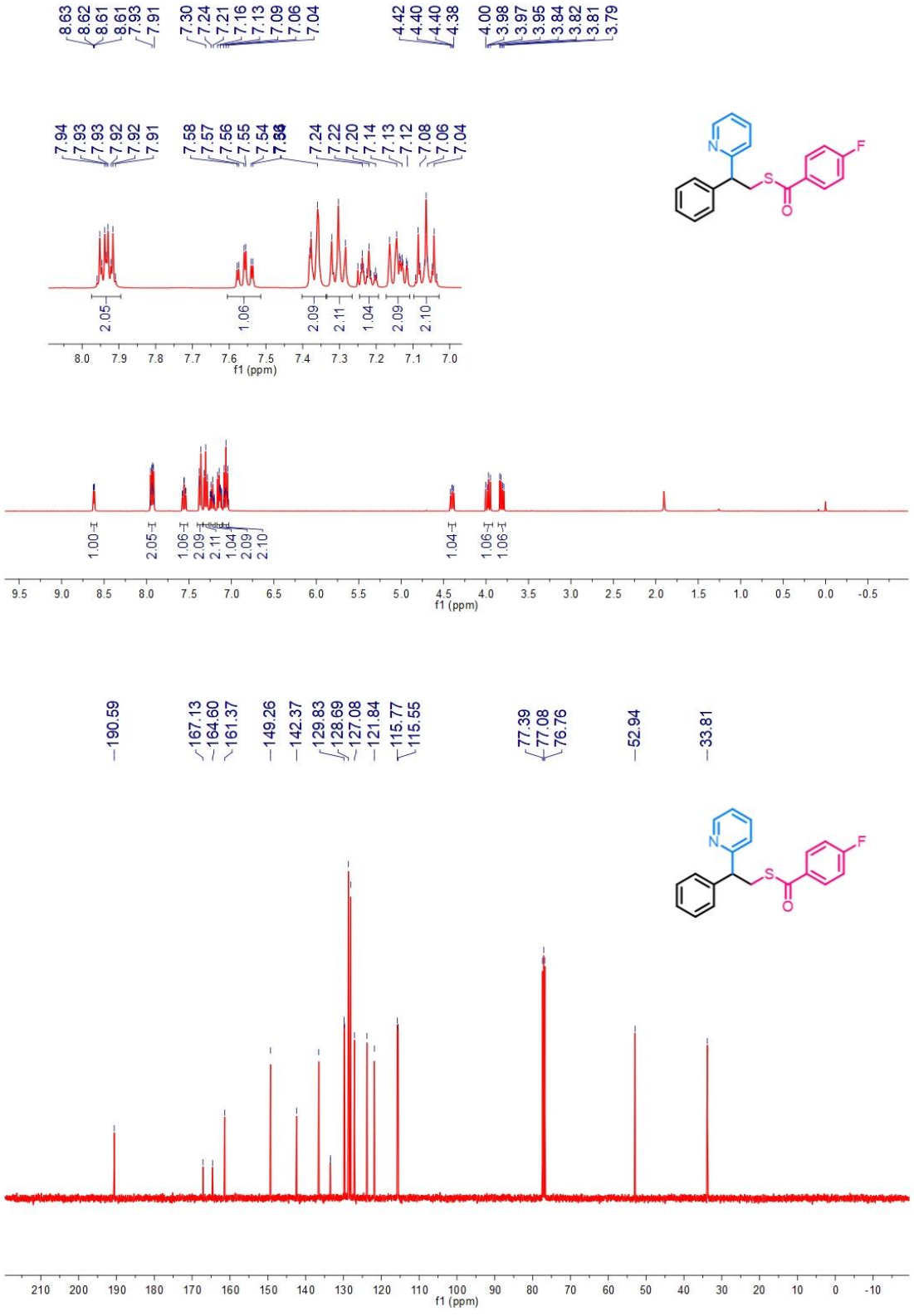


Fig. S52. The ^{1}H (400 MHz), ^{13}C (101 MHz) and ^{19}F (377 MHz) spectra for *S*-(2-phenyl-2-(pyridin-2-yl)ethyl) 4-fluorobenzothioate (**3ea**) in $CDCl_3$



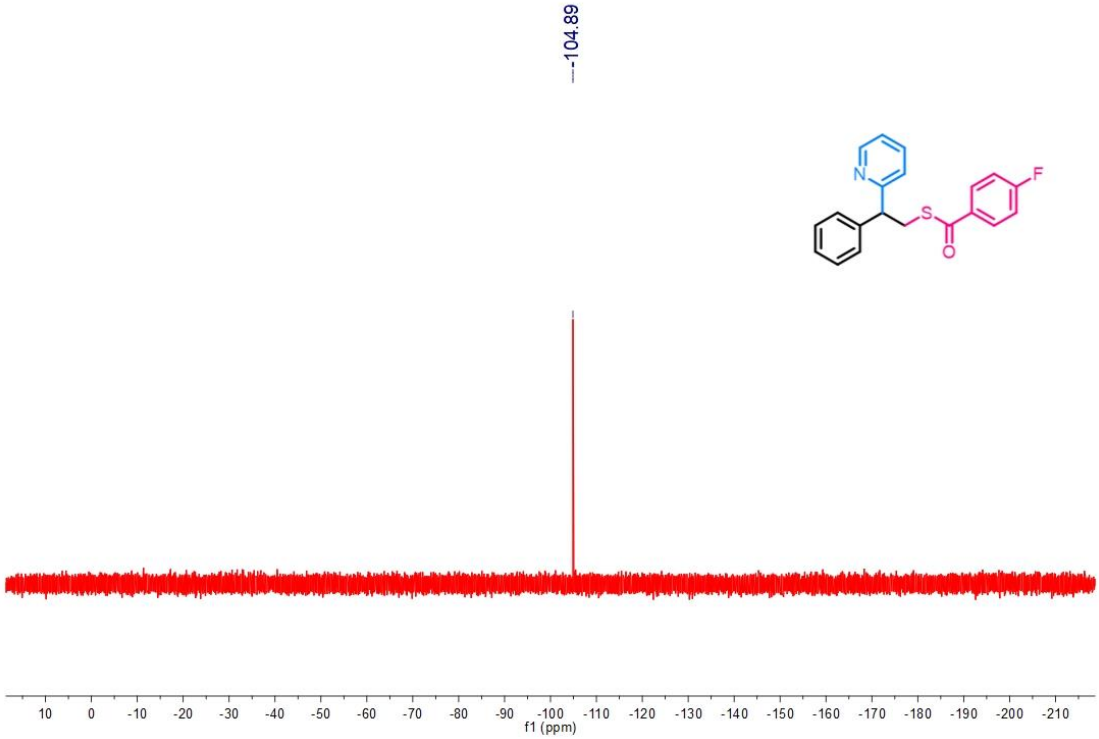

-104.89
N
S
O
F
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

Fig. S53. The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for *S*-(2-phenyl-2-(pyridin-2-yl)ethyl) 4-chlorobenzothioate (**3fa**) in $CDCl_3$

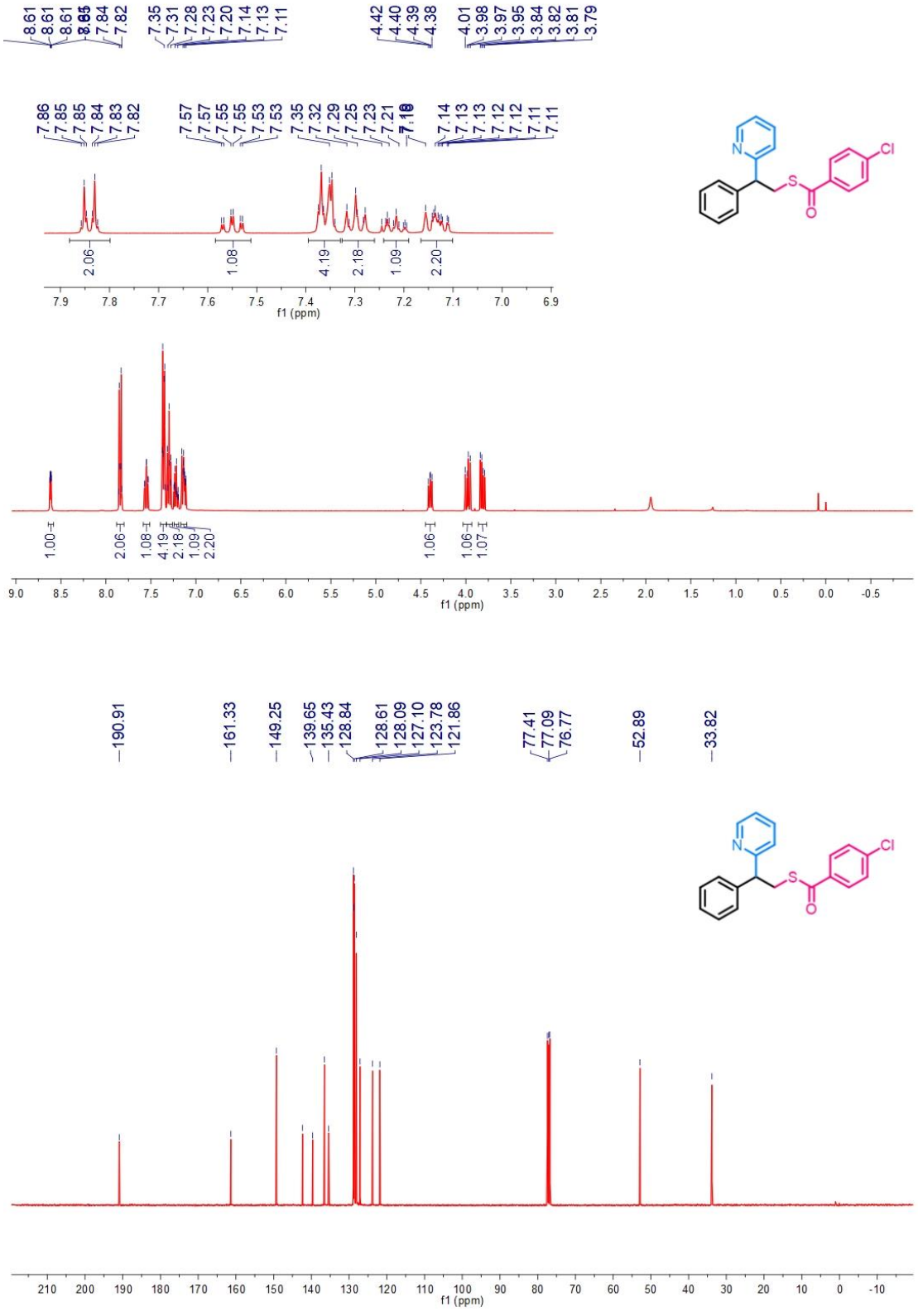


Fig. S54. The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for *S*-(2-phenyl-2-(pyridin-2-yl)ethyl) 4-bromobenzothioate (**3ga**) in $CDCl_3$

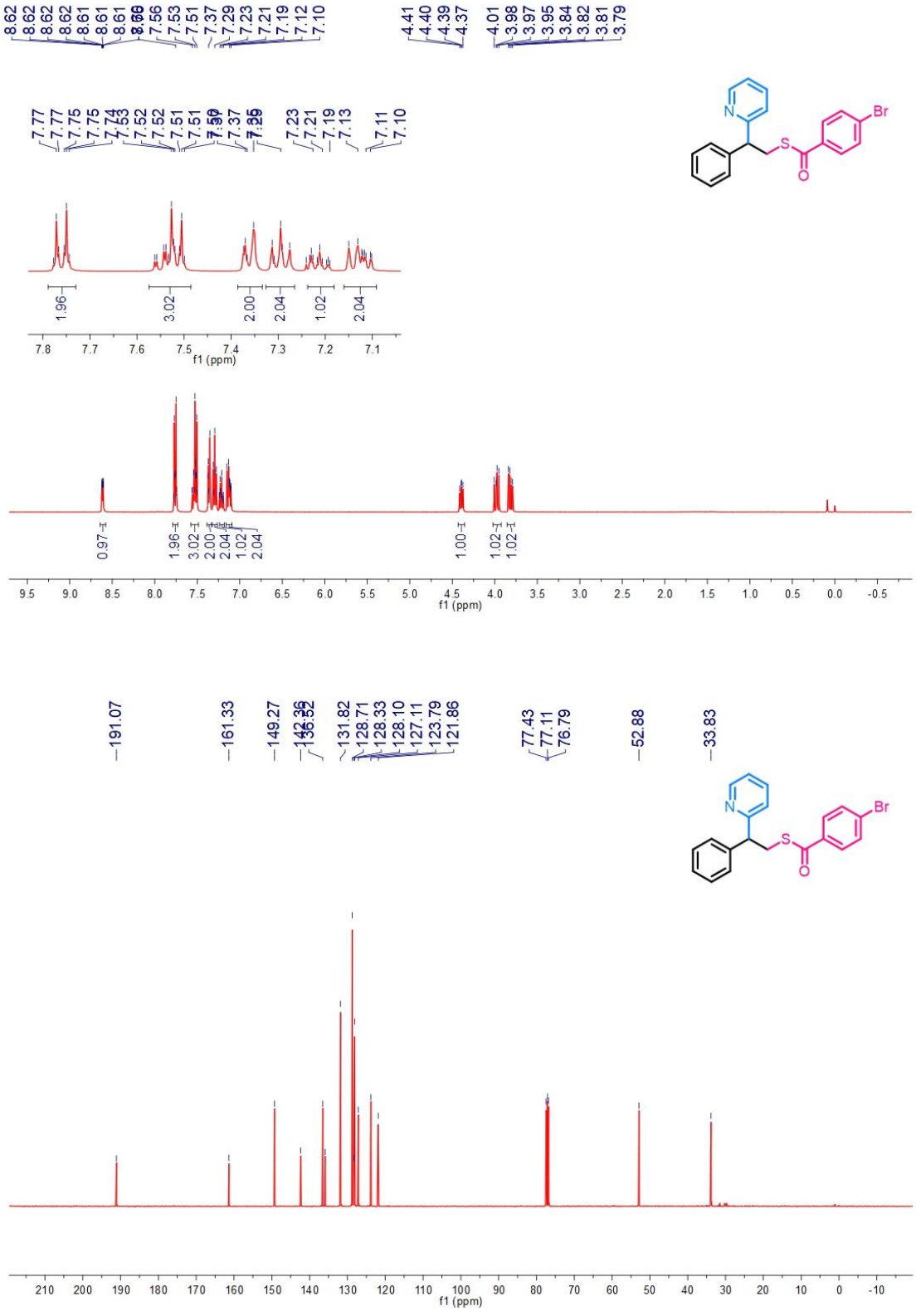


Fig. S55. The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for *S*-(2-phenyl-2-(pyridin-2-yl)ethyl) 4-iodobenzothioate (**3ha**) in $CDCl_3$

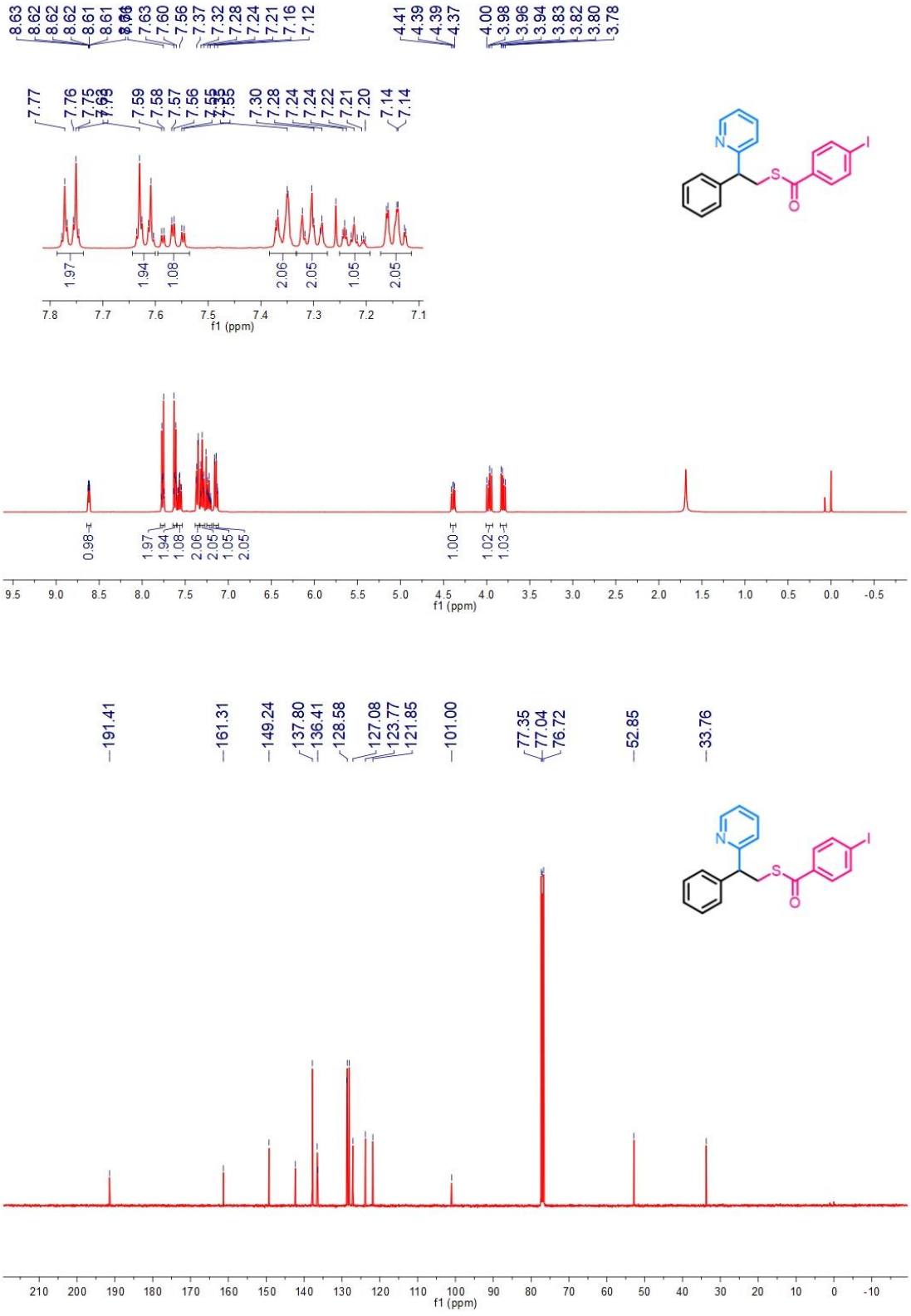
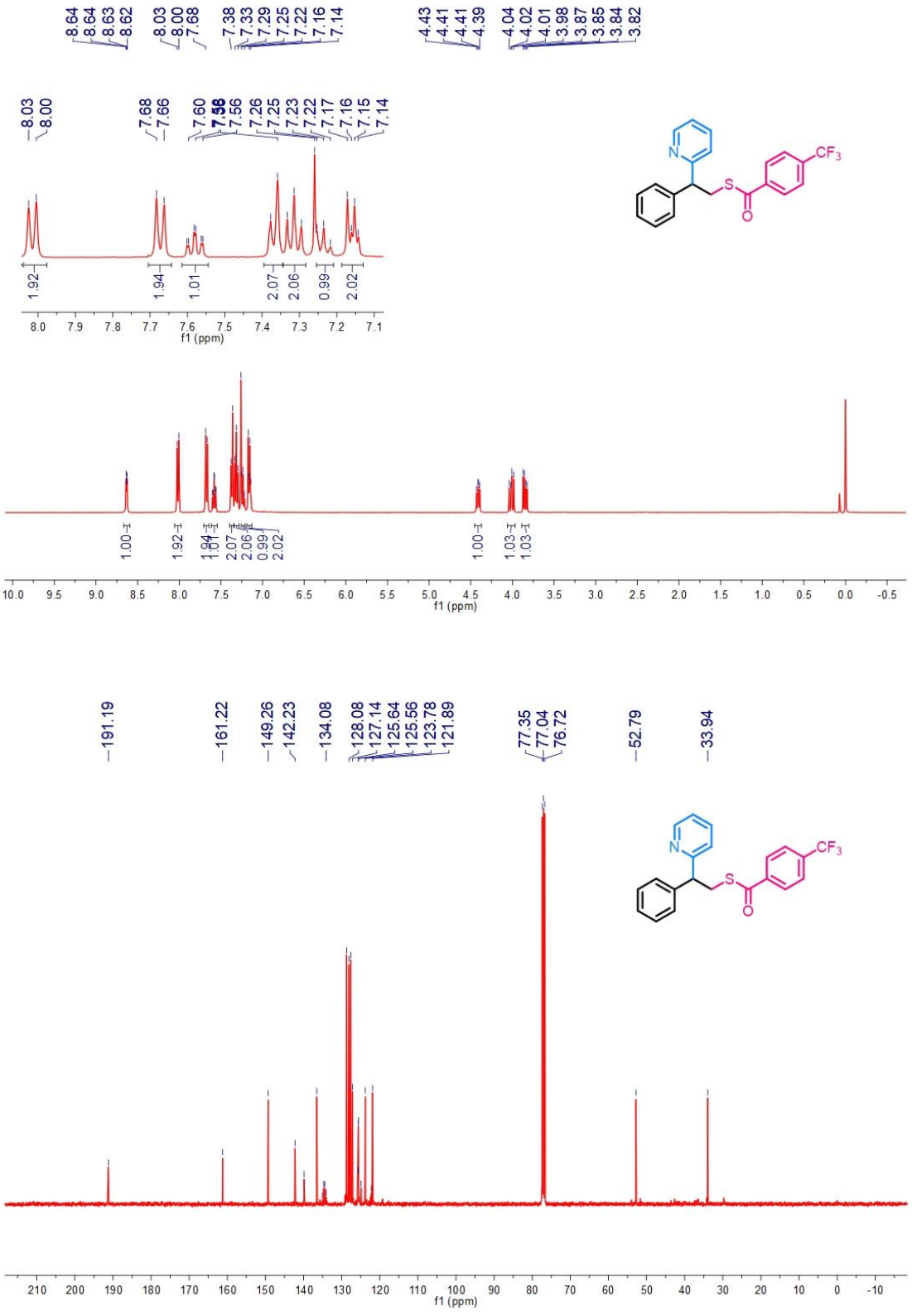


Fig. S56. The ^{1}H (400 MHz), ^{13}C (101 MHz) and ^{19}F (377 MHz) NMR spectra for *S*-(2-phenyl-2-(pyridin-2-yl)ethyl) 4-(trifluoromethyl)benzothioate (**3ia**) in $CDCl_3$



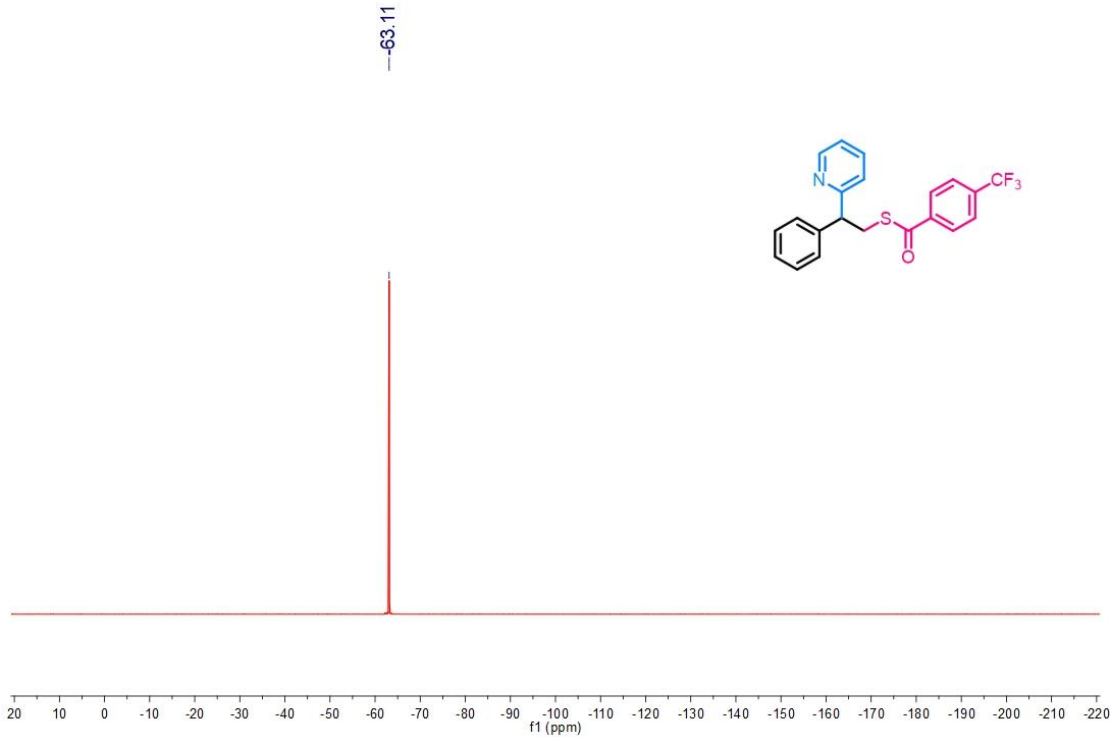
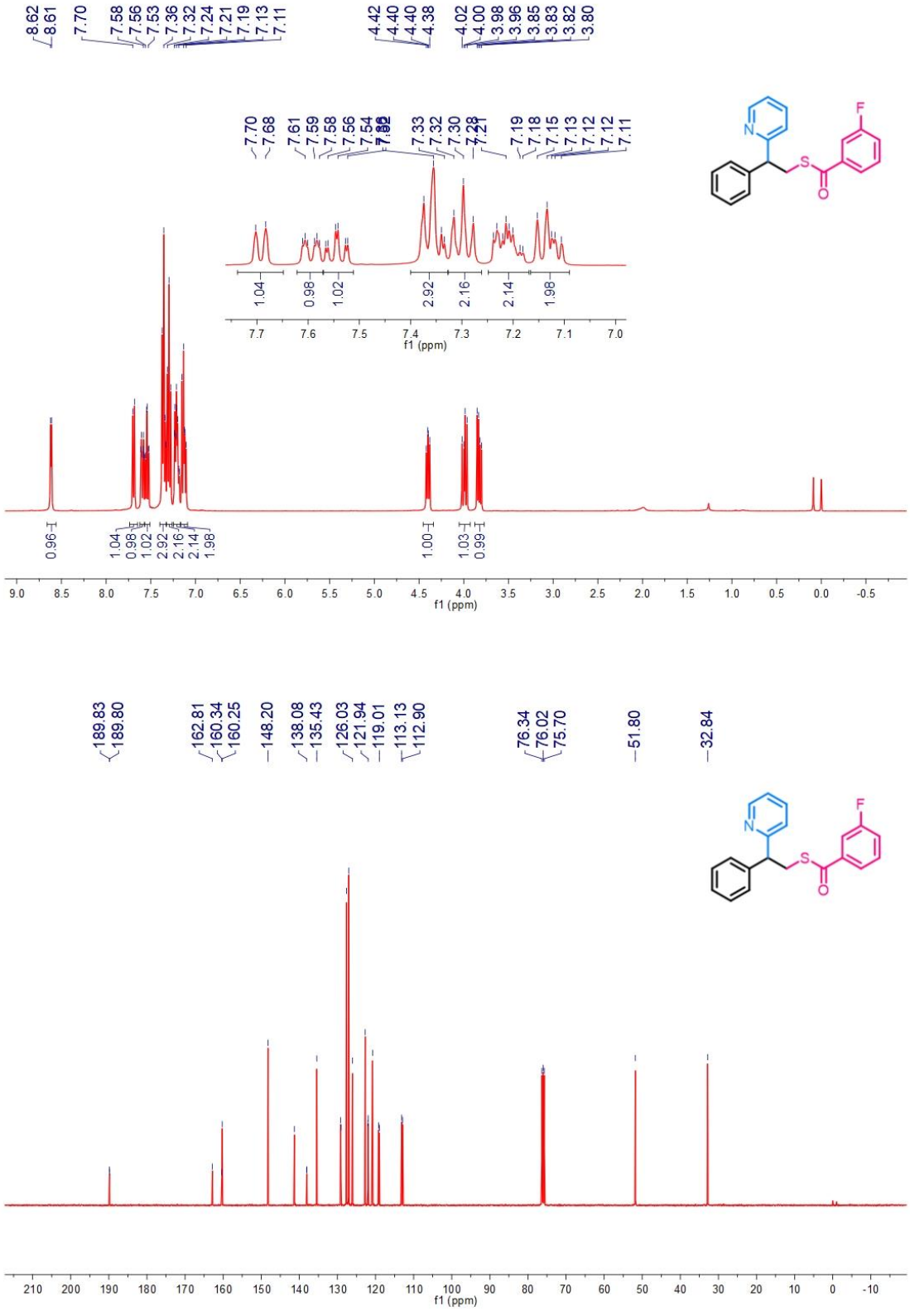

-63.11
N
S
O
CF3
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

Fig. S57. The ^{1}H (400 MHz), ^{13}C (101 MHz) and ^{19}F (377 MHz) NMR spectra for *S*-(2-phenyl-2-(pyridin-2-yl)ethyl) 3-fluorobenzothioate (**3ja**) in $CDCl_3$



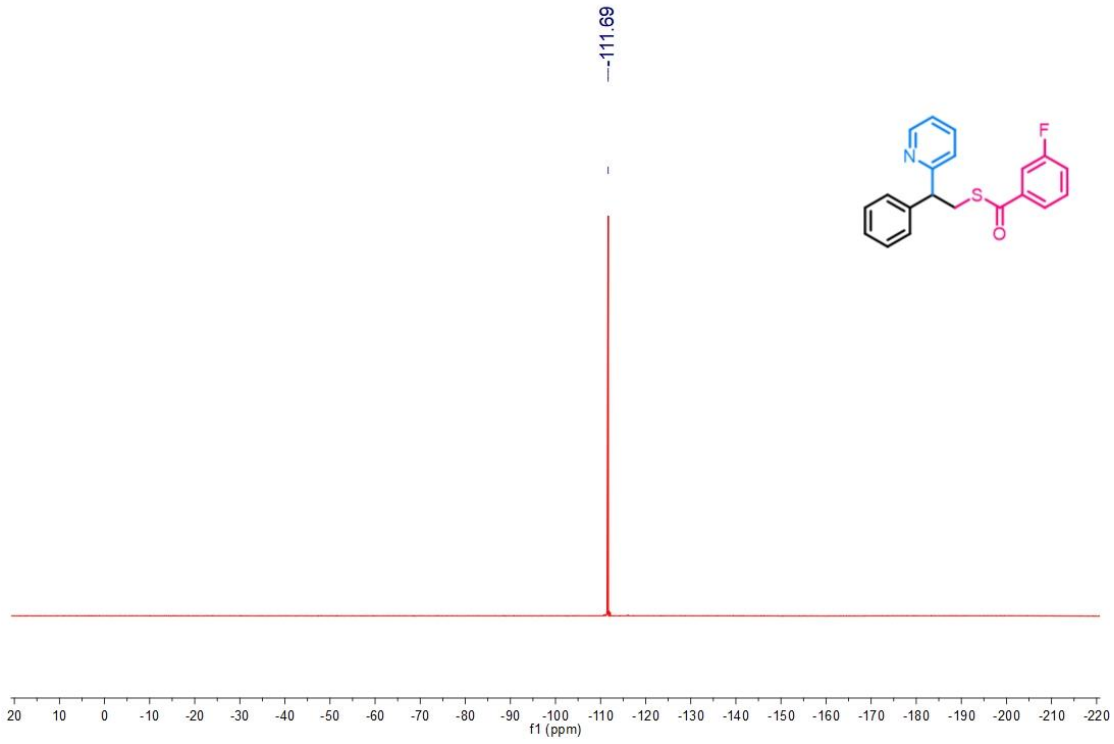

-111.69
N
F
S
O
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

Fig. S58. The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for *S*-(2-phenyl-2-(pyridin-2-yl)ethyl) 3,4-dimethoxybenzothioate (**3ka**) in $CDCl_3$

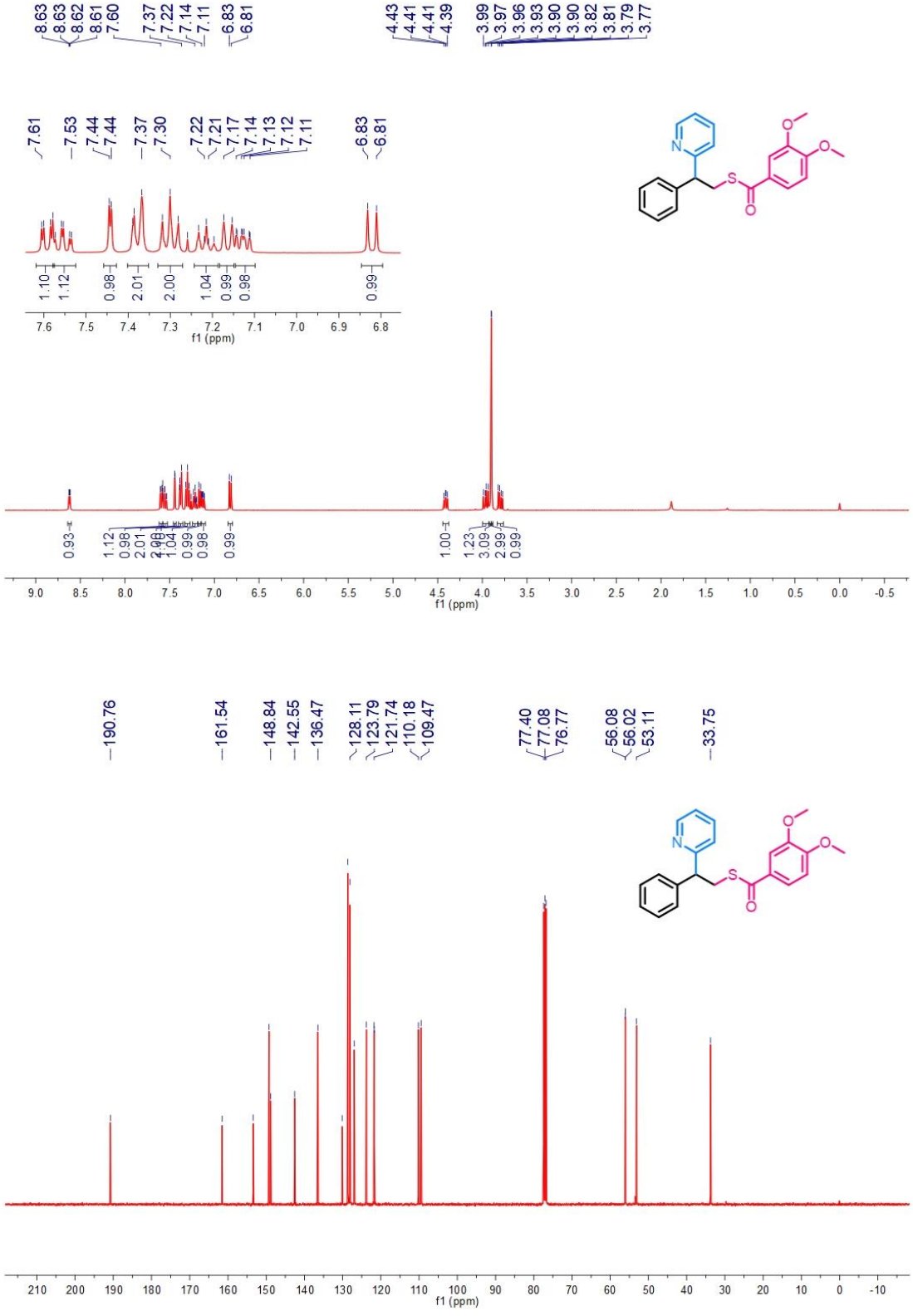


Fig. S59. The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for *S*-(2-phenyl-2-(pyridin-2-yl)ethyl) naphthalene-2-carbothioate (**3la**) in $CDCl_3$

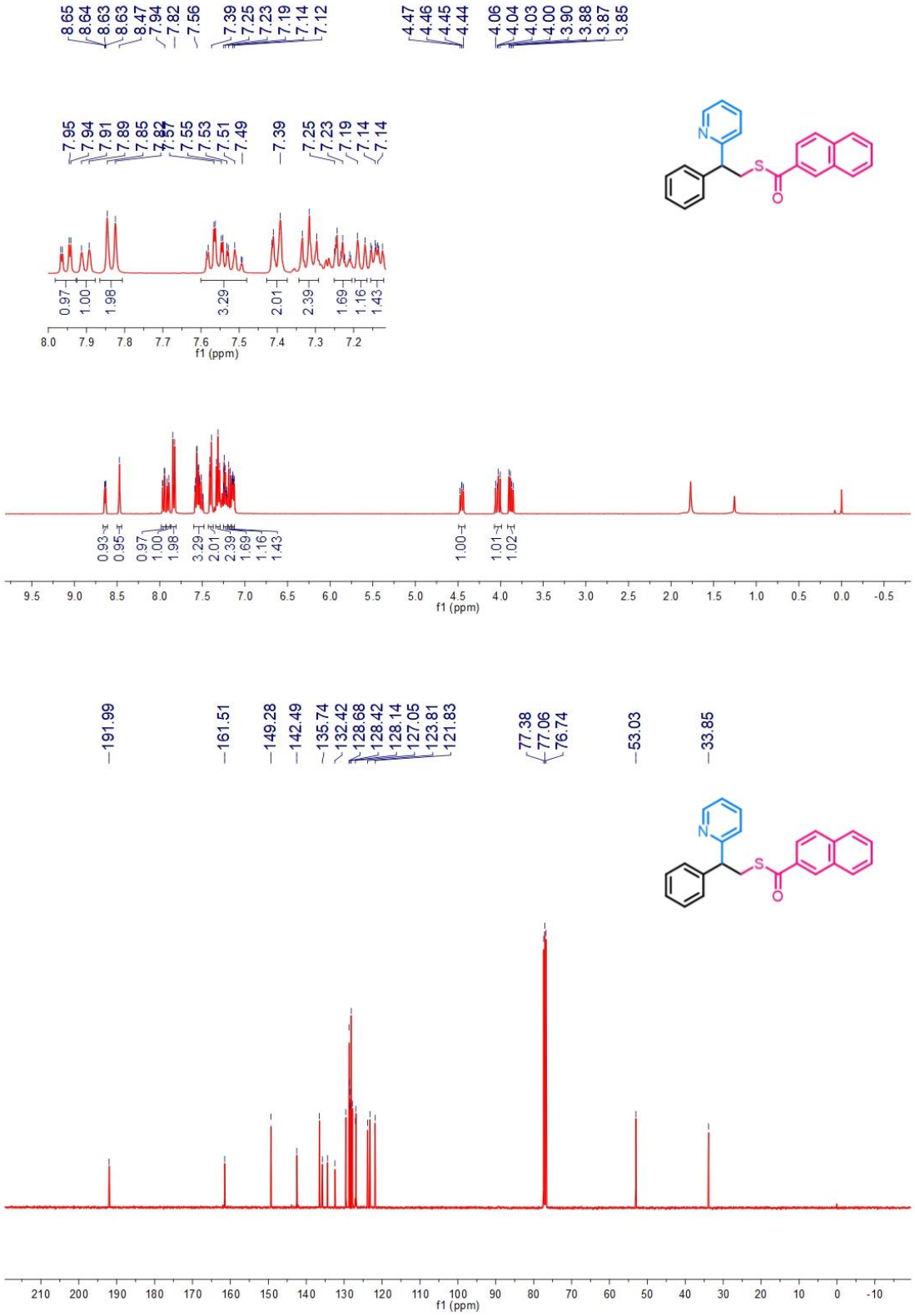


Fig. S60. The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for *S*-(2-phenyl-2-(pyridin-2-yl)ethyl) furan-2-carbothioate (**3ma**) in $CDCl_3$

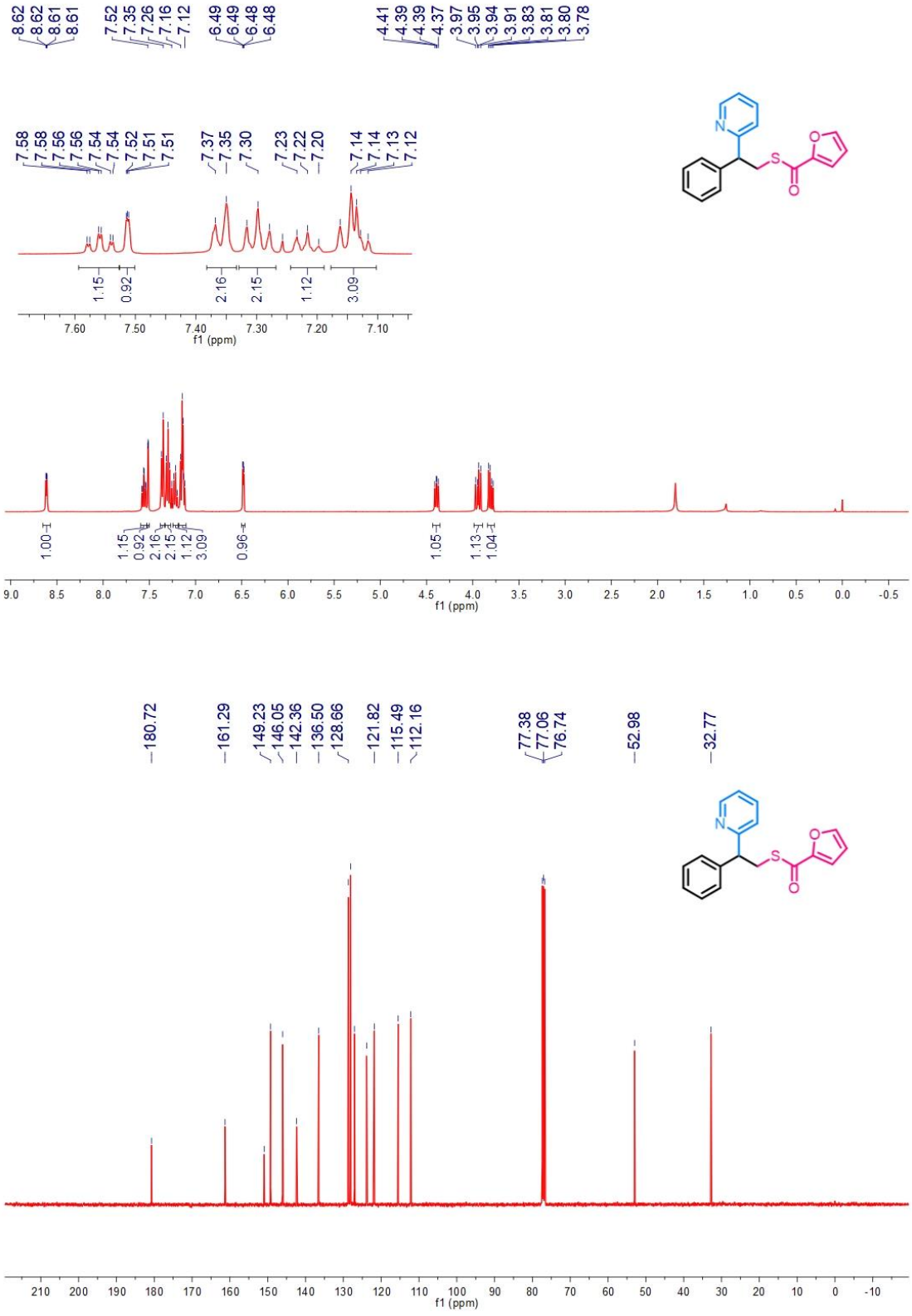


Fig. S61. The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for *S*-(2-phenyl-2-(pyridin-2-yl)ethyl) thiophene-2-carbothioate (**3na**) in $CDCl_3$

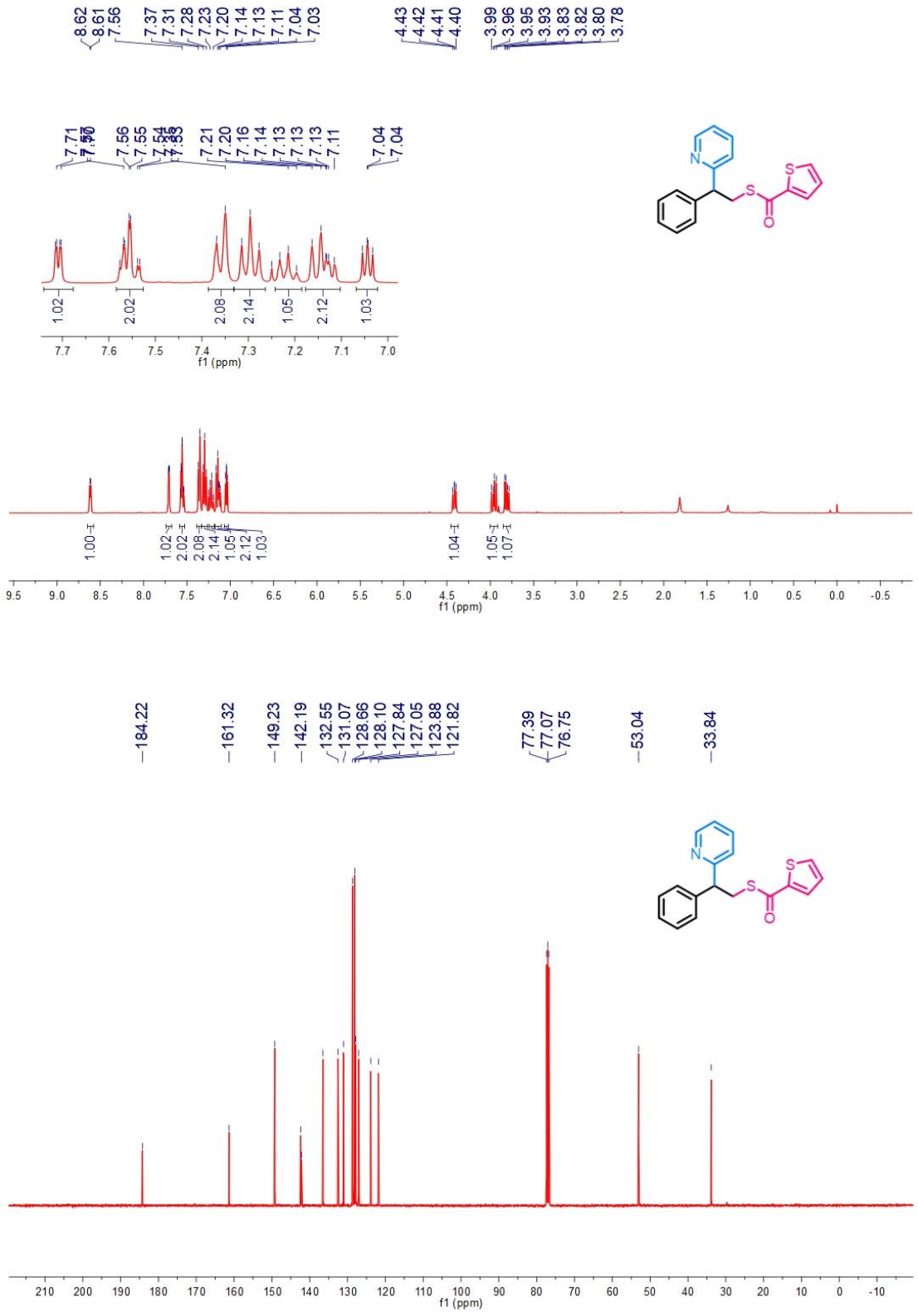
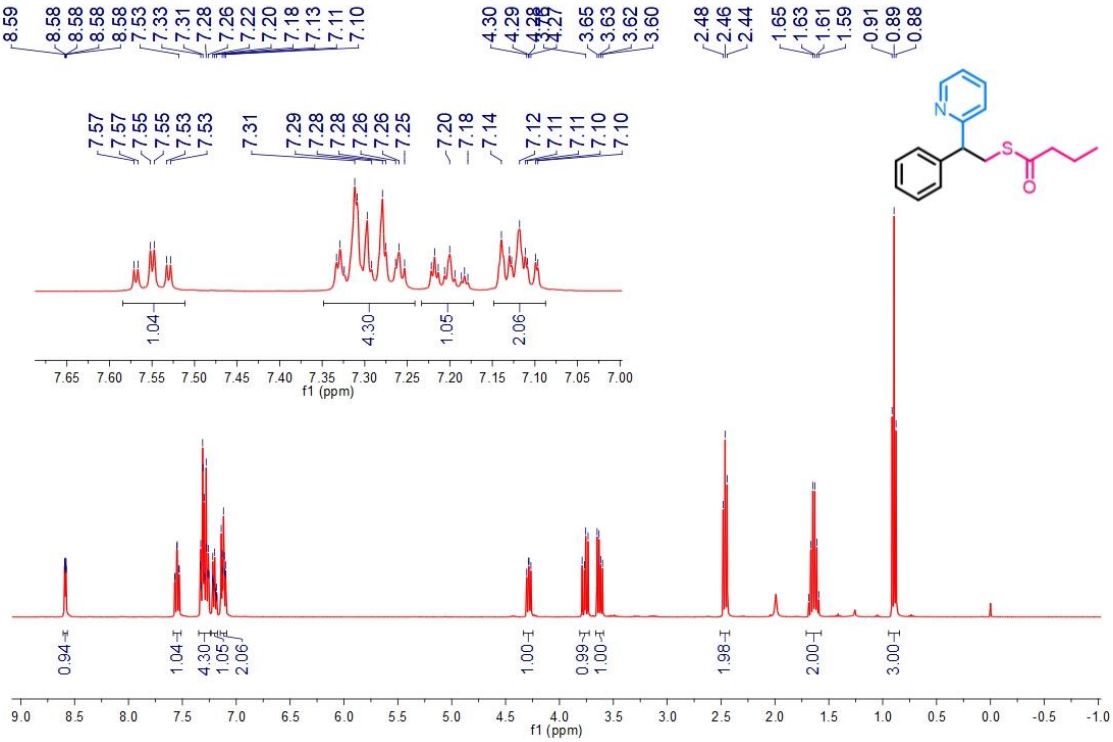


Fig. S62. The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for *S*-(2-phenyl-2-(pyridin-2-yl)ethyl) butanethioate (**3oa**) in $CDCl_3$



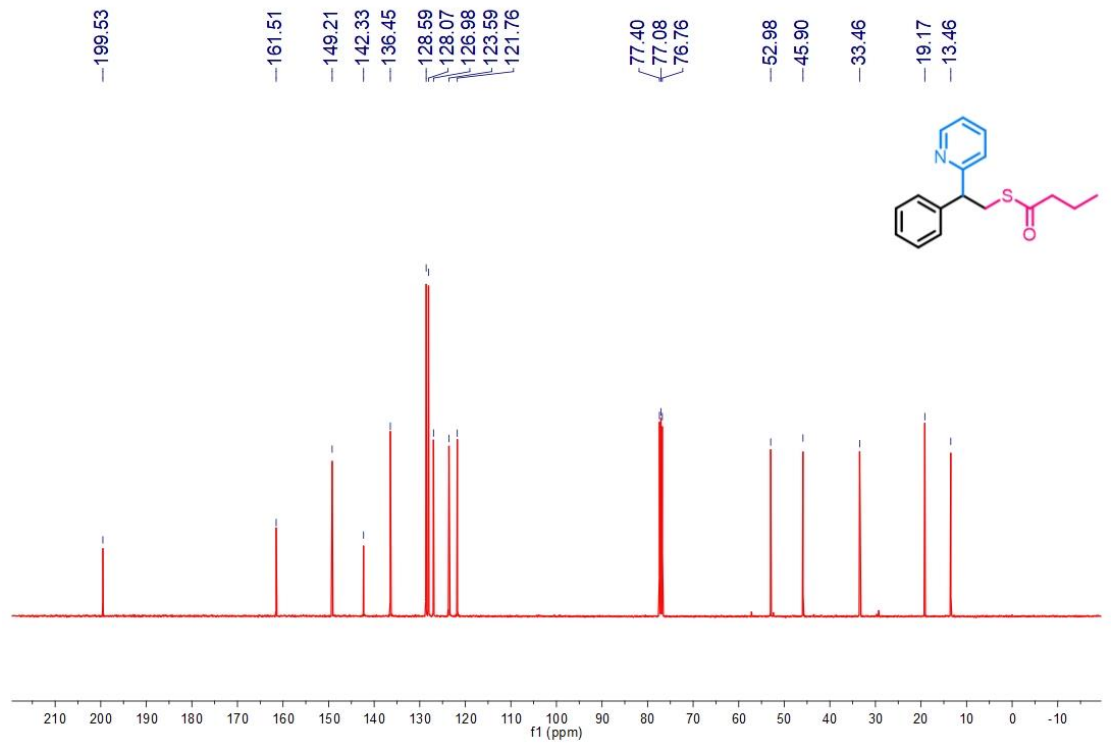


Fig. S63. The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for *S*-(2-phenyl-2-(pyridin-2-yl)ethyl) 2,2-dimethylpropanethioate (**3pa**) in $CDCl_3$

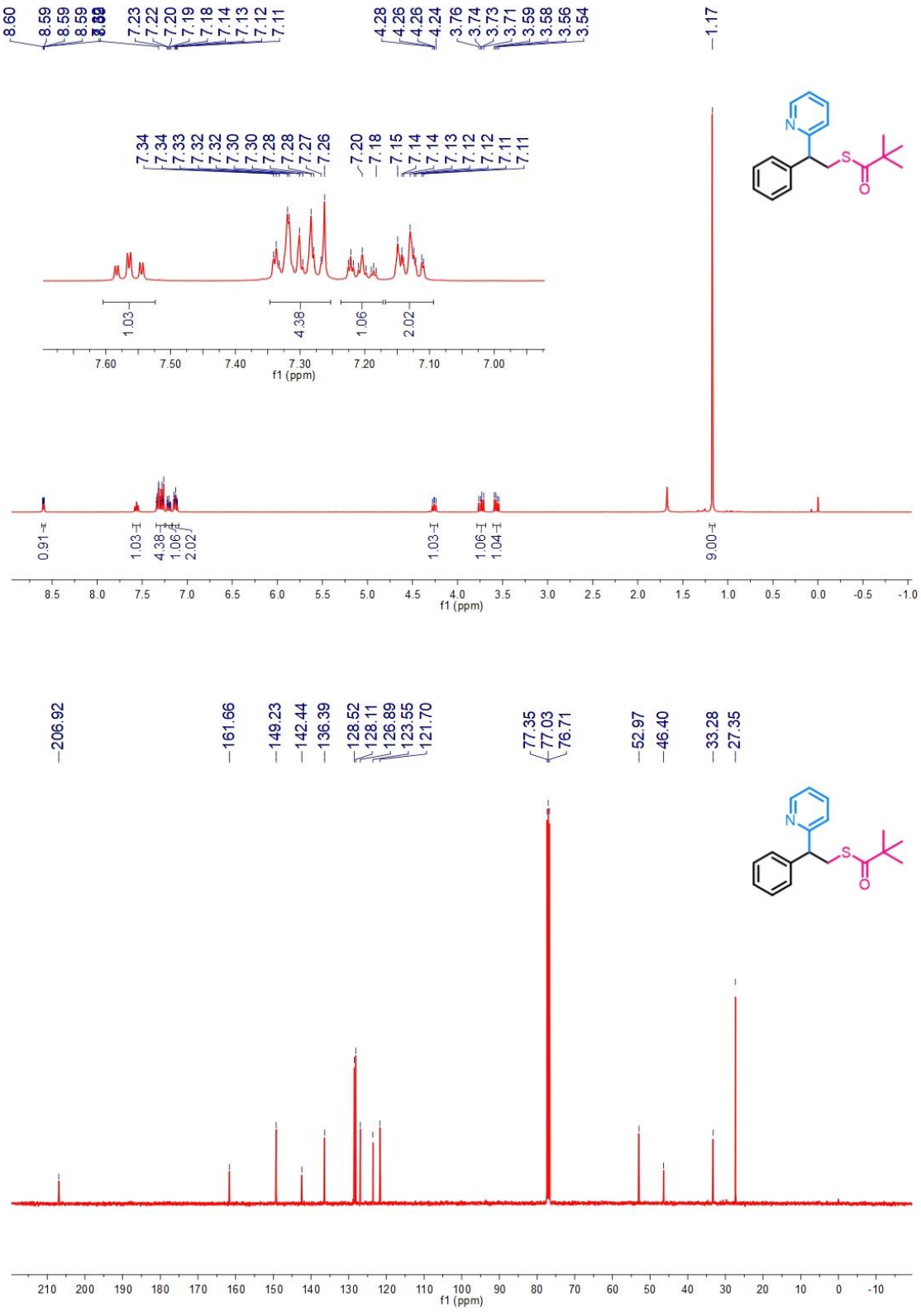


Fig. S64. The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for *S*-(2-(6-methylpyridin-2-yl)-2-phenylethyl) benzothioate (**3qa**) in $CDCl_3$

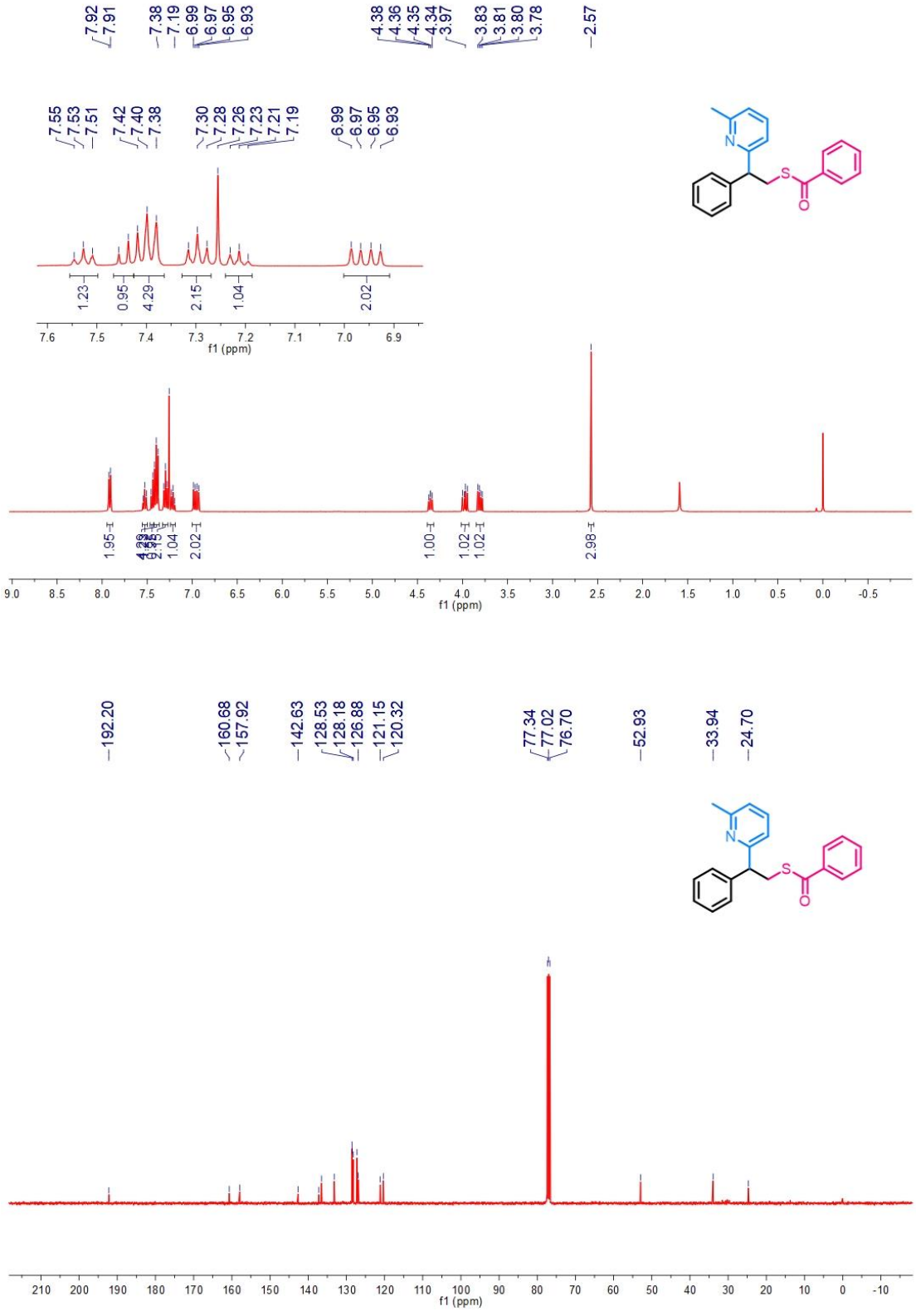


Fig. S65. The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for *S*-(2-(5-bromopyridin-2-yl)-2-phenylethyl) benzothioate (**3ra**) in $CDCl_3$

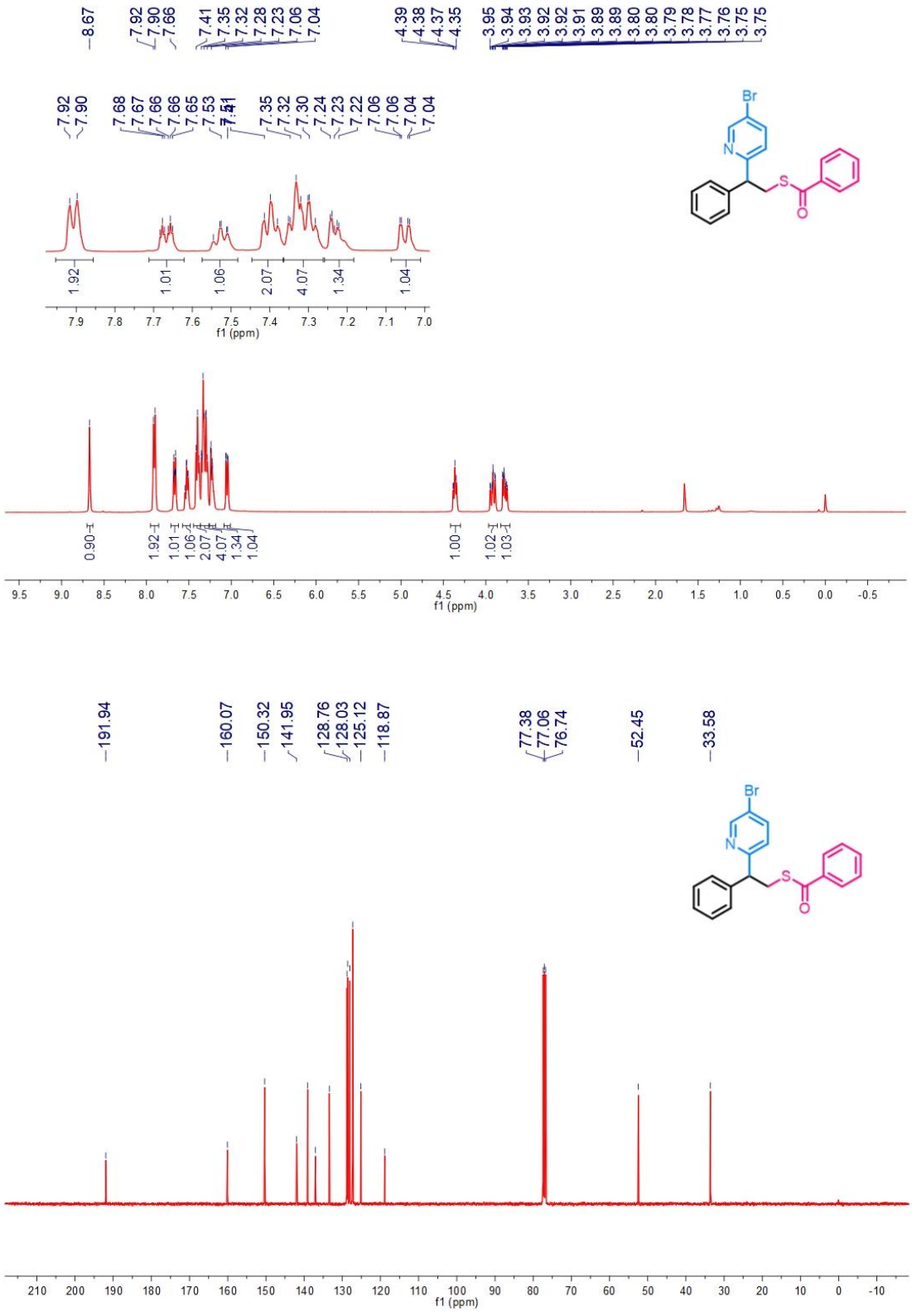


Fig. S66. The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for *S*-(2-phenyl-2-(pyridin-2-yl)ethyl) (2*R*)-2-(4-isobutylphenyl)propanethioate (**3sa**) in $CDCl_3$

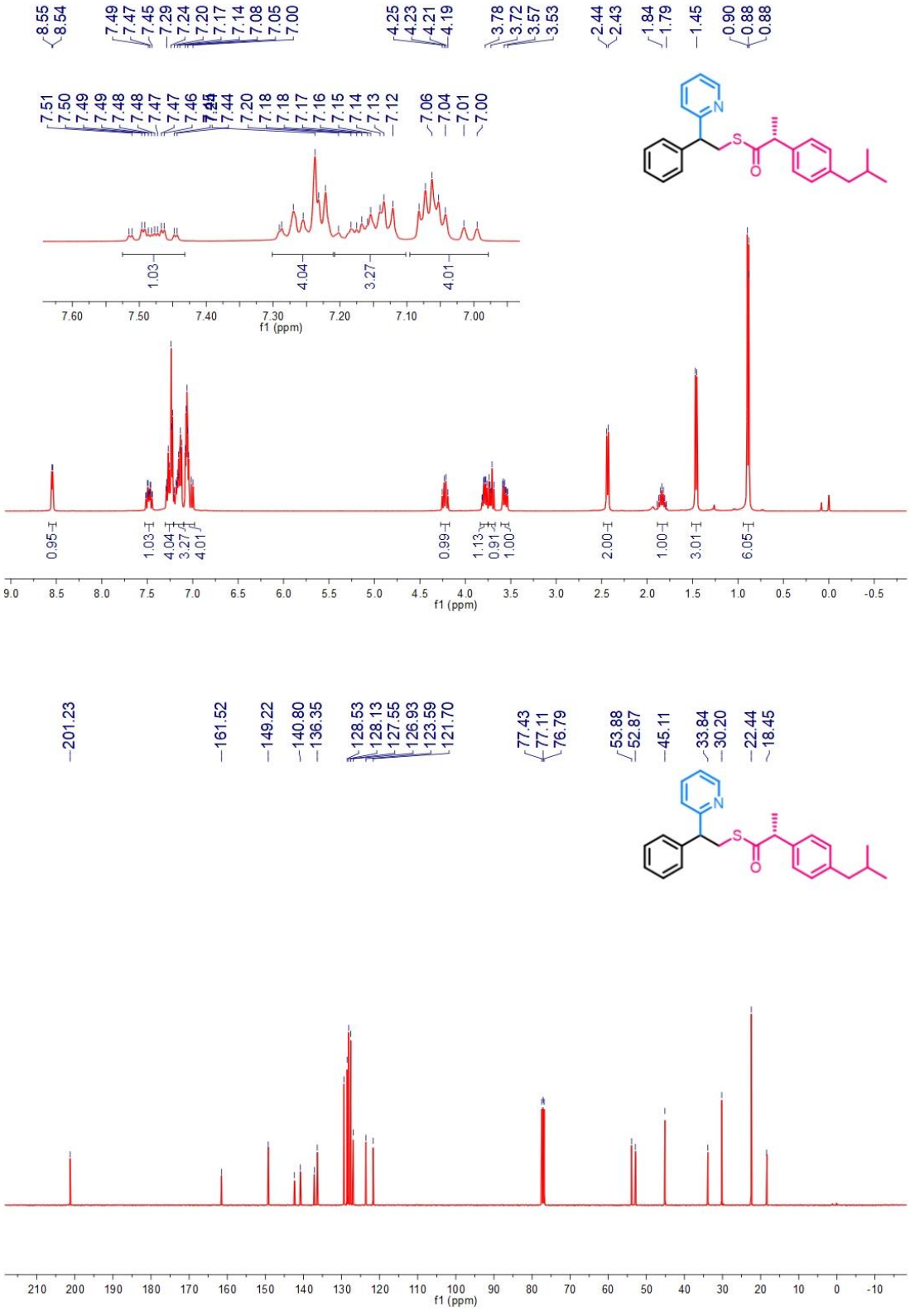


Fig. S67. The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for 2-(1-phenyl-2-(phenylthio)ethyl)pyridine (**4aa**) in $CDCl_3$

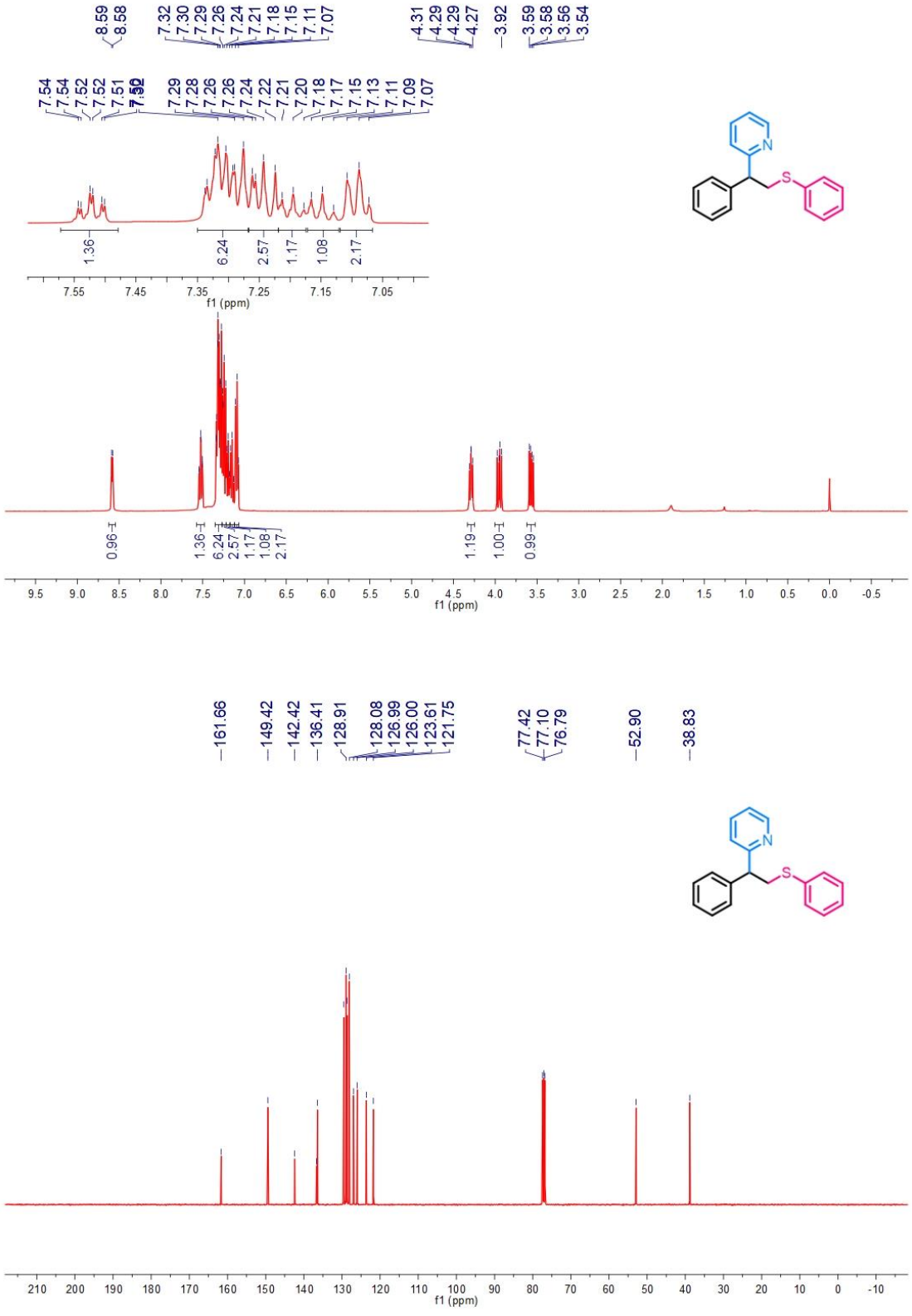
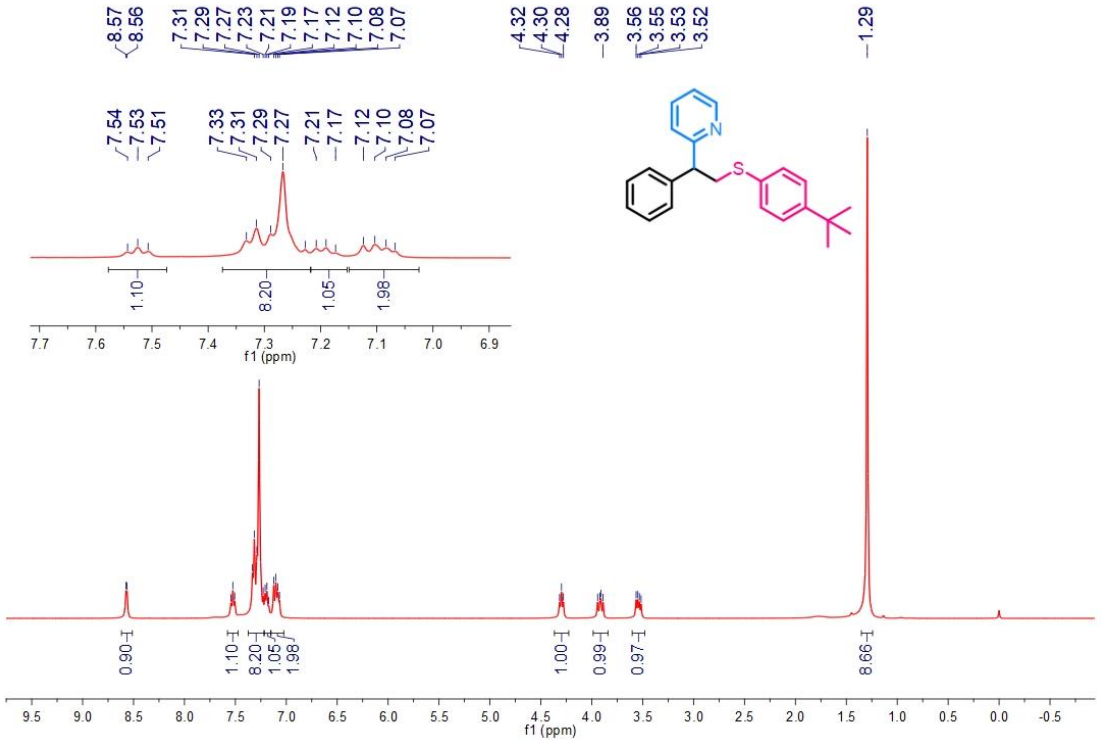


Fig. S68. The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for 2-(2-((4-(*tert*-butyl)phenyl)thio)-1-phenylethyl)pyridine (**4da**) in $CDCl_3$



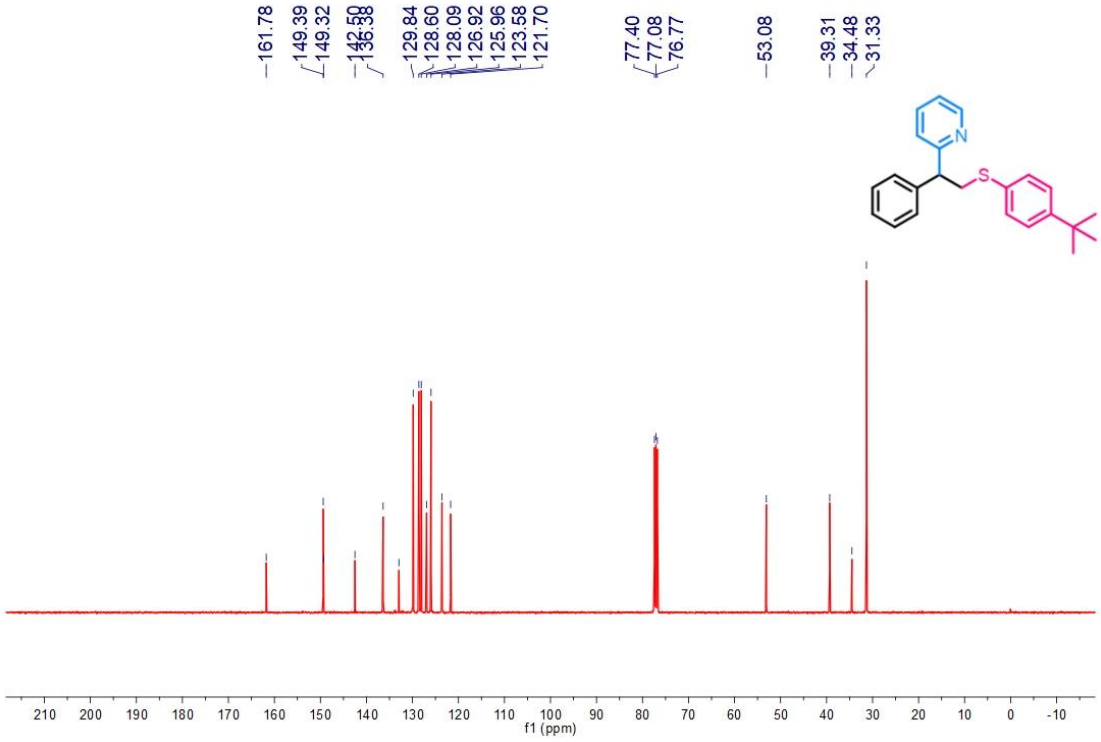


Fig. S69. The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for 2-(2-(phenylthio)-1-(*p*-tolyl)ethyl)pyridine (**4ab**) in $CDCl_3$

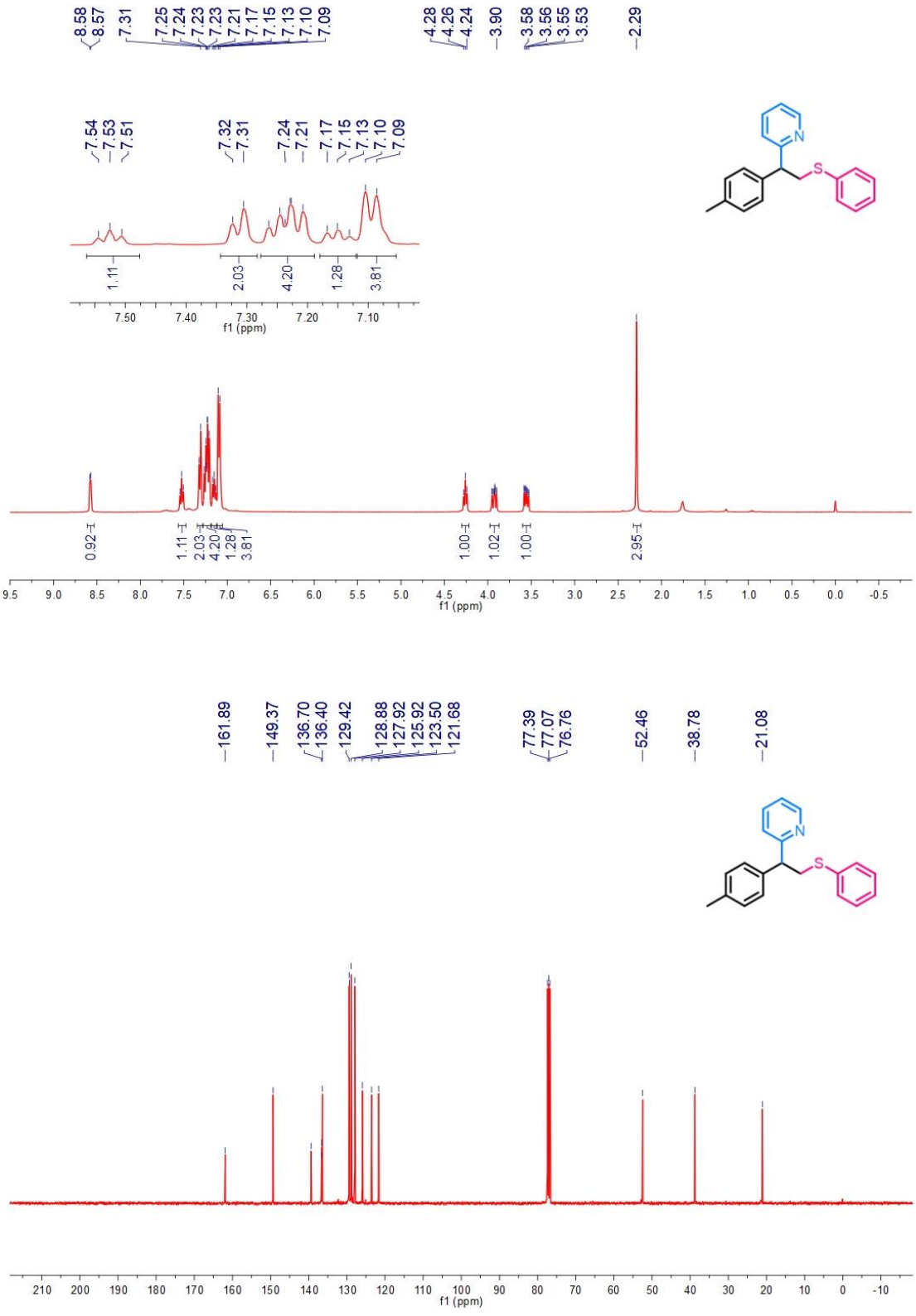


Fig. S70. The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for 2-(1-(4-bromophenyl)-2-(phenylthio)ethyl)pyridine (**4ag**) in $CDCl_3$